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LEE A. DUBRIDGE, CONSULTING EDITOR

PHOTOELECTRIC PHENOMENA

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Dr. F. K. Richtmyer was consulting editor of the series from its inception in 1929 until his death in 1939.

PHOTOELECTRIC PHENOMENA

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PREFACE

The output of theoretical and experimental results in physics grows at an ever increasing rate. The task of keeping abreast of recent developments becomes correspondingly more and more difficult. There is therefore ample justification for the publication of any book whose purpose is to give a concise yet comprehensive survey of one of the many fields of physics. For those merely wishing to obtain a general idea of the recent progress in a particular field, a book of this kind should save many a tiresome search through a voluminous literature. For those actually working in the field such a book justifies itself if it provides a fairly complete summary of the experimental methods and results, and of the prevailing theories, as well as a time-saving sign post to the original papers in the subject. For those interested in the technical branches of the subject, the book should serve as a guide to the fundamental physical principles which underlie the engineering and commercial applications.

It has been our aim to prepare such a book covering the field of Photoelectricity. The above considerations as to the possible value of the book have served to offset the discouraging knowledge, which must haunt the writer of any book on modern physics, that many of the results and conclusions which were quite acceptable at the time of writing may be questioned, or even superseded, by the time of publication, while many more will certainly be out of date within a very short time thereafter. Nevertheless a milestone, even after it has been passed, serves useful purpose if it shows what ground has already been covered, and particularly if it serves as an inspiration to a few, at least, to push on more rapidly to goals which lie ahead.

Although some researches were carried out in the photoelectric field during the last century, interest in it has been increasing steadily and, in particular, the past decade has witnessed an amazing development. On the experimental side, improvements in technique have made possible considerable advances in the study of clean metal surfaces and of surfaces covered with alkali films. On the theoretical side, the photoelectric effect, which has long been one of the cornerstones of the quantum theory of radiation, now finds itself closely intertwined with recent advances in quantum mechanics and the newer electron theory of metals. Theoretical physicists have repeatedly turned to photoelectric experiments for verification of their results, and have in turn revolutionized many of our ideas as to the nature of the photoelectric process. The field of photo-

conductivity, which a few years ago consisted of a mass of unrelated and discordant observations, has in the past ten years been skillfully explored and has now been placed on a sound scientific basis. Chapter VIII of the present volume is, we believe, the first summary of this work which has appeared in English. Finally, with the development of the modern highly sensitive photoelectric cell, the technical applications of the photoelectric effect have multiplied by leaps and bounds. The time seems not far distant when the photoelectric cell will become as well-known and as important a commercial instrument as the thermionic vacuum tube—to which it owes a large share of its practical usefulness. It is the purpose of the present volume to survey as completely as possible all of these lines of development.

The general plan of the book will be at once evident from an inspection of its Table of Contents, but a brief explanation of its general arrangement may not be out of place. Following a short Introduction, four chapters are devoted to a presentation of the experimental results having to do with the problem of the emission of electrons from metal surfaces when illuminated by visible or ultra-violet light. The theoretical problems connected with this subject are discussed in Chapter VI, a chapter which the authors, who are not theoretical physicists, hesitated to attempt. However, photoelectric results have played such an important rôle in guiding the development of our theories of matter and radiation, and the latter have in turn served as such a powerful stimulus in directing the course of photoelectric research, that no account of the subject would seem to us complete without a discussion of its theoretical background.

Chapters VII and VIII are devoted to the "volume photoelectric effect," the former taking up the photoionization of gases, and the latter the important subject of photoconductivity in solids. Photovoltaic effects and photoelectric effects in liquids and insulators are treated in the next two chapters, followed by Chapter XI on the photoelectric effects of X-rays and gamma rays. This subject is one which deserves a more extended treatment than the present authors are able to give. We have contented ourselves with a brief review of its principal aspects, particularly those which are closely related to effects observed in the optical region.

Chapter XII on experimental technique was intended as a guide to those who are beginning research in photoelectricity and to those who are applying photoelectric methods in other fields. Some of the data collected should also be of use to more experienced experimenters in the field. We have tried in particular to emphasize those points which are not usually fully described in published papers.

We had originally planned a more extended account of the applications of the photoelectric effect than is contained in Chapter XIII.

However, while our manuscript was in preparation three books on this subject appeared, all by authors far more intimately acquainted with the field than ourselves. It seemed unnecessary to cover this ground again, particularly since it became evident that our discussion of the purely physical aspects of photoelectricity would fill a sizable volume. We have endeavored to describe the rôle played by the photoelectric cell in the more important commercial developments, without going into a detailed discussion of the engineering problems involved.

In conclusion, it is a pleasant duty to record our appreciation of the valuable assistance given to us during the preparation of the manuscript by many investigators in the field of photoelectricity. We are particularly grateful to the following physicists who have made available to us, some months in advance of their publication, results of their investigations or of investigations carried out in their laboratories: Professor C. E. Mendenhall, Professor R. H. Fowler, Dr. N. R. Campbell, and Dr. K. S. Gibson. Chapter III was submitted in manuscript to Professor C. E. Mendenhall, and Chapter VI to Professor E. U. Condon, Professor V. Rojansky, and Dr. J. A. Becker, all of whom gave us the benefit of their constructive criticism. We should also like to acknowledge our indebtedness to Dr. H. E. Ives, Dr. R. Pohl, Dr. B. Gudden, Professor F. W. Loomis, Dr. S. Dushman, Dr. L. R. Koller, Professor G. E. M. Jauncey, Professor R. S. Mulliken, Dr. J. A. Van den Akker, and many others whom we have consulted on specific points. We have found useful Gudden's "Lichtelektrische Erscheinungen" (Julius Springer, 1928) and Becker's monograph on photoelectricity in Vol. XXIII of the Wien-Harms "Handbuch der Experimentalphysik" (Leipzig Akademische Verlagsgesellschaft, 1928), both of which appeared during the preparation of this book. Thanks are due to Dean A. L. Clark of Queen's University, Kingston, Canada, for permission to use the Physics Library there during the past three summers. Finally we wish to thank Messrs. W. W. Roehr, P. S. Williams, and G. G. Harvey for their assistance in correcting manuscript and proof, and Mrs. J. H. McMillen for her careful typing of the manuscript.

Arthur Llewelyn Hughes.
Lee Alvin DuBridge.

St. Louis, Mo.,
January, 1932.

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PHOTOELECTRIC PHENOMENA

CHAPTER I

INTRODUCTION

A photoelectric effect is one in which the absorption of radiation by matter produces an electrical change. Inasmuch as light is an electromagnetic phenomenon and since matter, according to our present theories, consists solely of protons and electrons, it is evident that *every* interaction between radiation and matter must necessarily involve some electrical change in the latter, either as an intermediate step or as a final result. To include all such effects within the field of photoelectricity would make it coextensive with the whole field of optics and the study of radiation in general. It is therefore customary to include among photoelectric phenomena only those effects in which the electrical changes are directly observable, and not merely inferred from other phenomena by means of some theory. Since electrical effects are usually directly observed only when there is an actual separation of positive and negative electricity, we may define a photoelectric effect as one in which radiation causes a separation of electrons from atoms so that an electric current may be caused to flow. This definition allows us to rule out of the domain of photoelectricity all phenomena such as the reflection, refraction, absorption, interference, and polarization of light (or X-rays), and almost the whole field of photochemistry. In the field of photochemistry, for example, radiation may produce an *excitation* of atoms or molecules but does not in general produce *ionization*, *i.e.*, the separation of electrons from atoms. We also rule out all phenomena in which the electrical changes observed are due merely to the *heating effect* of the radiation and the consequent rise in temperature of the absorbing material.

Even after the above exclusions are made, the domain of photoelectricity is still a large one, for it is found that photoelectric effects may apparently be produced by radiation of any wave-length from the shortest cosmic rays to the long infra-red rays. (We must exclude all phenomena having to do with radio waves!) In the present volume, therefore, we shall confine our attention primarily to the photoelectric effects of visible and ultra-violet light, though for the sake of completeness

we have discussed briefly (in Chapter XI) some of the effects observed with X-rays and gamma rays. The fundamental laws governing photoelectric phenomena are, however, the same for all wave-lengths.

Phenomena involving the release of electrons by light fall naturally into three main groups, each of which developed for many years independently of the others. As is inevitable in a rapidly growing field, however, the lines of demarcation between them are being obliterated and it is now becoming increasingly evident that they all depend on the same fundamental basis. The three divisions are:

1. Surface photoelectric effects.
2. Volume photoelectric effects.
3. Photovoltaic effects.

The essential feature of the *surface photoelectric effect* is the release of electrons by light at the boundary between a solid or liquid on the one hand, and usually a gas or vacuum on the other. In a few cases, however, photoelectric effects have been observed at the boundary between a metal and a transparent insulating liquid or solid.

A *volume photoelectric effect* involves the separation of electricity throughout a finite volume and is observed as a change in the conductivity of the material when illuminated (independent of the heating effect of the radiation). The effect is therefore frequently termed *photoconductivity.* We cannot, of course, expect to detect a volume photoelectric effect in metals since their natural conductivity is too high. Photoconductivity is, however, observed in gases and in certain insulators or partial conductors (liquid or solid).

A *photovoltaic effect* is the generation of an *electromotive force* in a circuit containing the sensitive material, so that a current may flow without the assistance of a battery. In the two other types of photoelectric effect a current will flow only when an external battery is employed to direct the flow of the released electrons.

We may well begin our review of this subject with a brief history of photoelectric phenomena. The discovery of the surface photoelectric effect was made by Hertz[1] in 1887. It is of interest to point out that the physicist who is best known for his classic investigation which brilliantly verified the electromagnetic theory of light also, in the course of this same investigation, uncovered a new effect which was destined to play an important rôle in providing the experimental foundation for the quantum theory! In the course of his experiments on electrical resonance Hertz observed that the length of the spark which could be induced in an auxiliary circuit was considerably reduced when the spark gap was shielded from the light of the spark in the primary circuit. He found on further study: (1) that the change in spark length in the auxiliary circuit is not caused by any electrical effect but is due solely to the illu-

[1] H. Hertz, *Ann. d. Phys.*, **31**, 983 (1887).

mination of the electrodes; (2) that it is due only to the ultra-violet portion of the light; and (3) that the effect is most marked when the negative electrode is illuminated.

These results led to a series of fundamental experiments by Hallwachs.[1] He found that a polished zinc plate when insulated and connected to an electroscope would retain a positive charge but would rapidly lose a negative charge when illuminated by light from a carbon arc. The effect disappeared if a glass screen was placed in front of the arc, showing that only the ultra-violet light was responsible for the discharge of the plate. It was thus established that the *surface photoelectric effect consists in the emission of negative electricity from the illuminated plate* when the field in its vicinity is such as to allow the charges to escape. The same effect was observed for many other substances. As a tribute to Hallwachs' fundamental investigations, the surface photoelectric effect is often, particularly by German writers, referred to as the "Hallwachs effect."

In 1889 Elster and Geitel published the first of a long series of papers on photoelectricity, a series which was to single them out as the leading pioneers in this new field. Their first contribution[2] was to show that certain metals (potassium, sodium, zinc, and aluminum) when amalgamated with mercury became photoelectrically sensitive to *visible* as well as ultra-violet light, although others, such as tin, copper, and iron, remained inactive. In air at atmospheric pressure an insulated plate of zinc was found to acquire a potential of +2.5 volts when illuminated. This is perhaps the first experiment to suggest that the particles of electricity were ejected from the plate with a small but finite velocity, although Elster and Geitel at the time did not consider such an interpretation. (The presence of the air introduces complications which were eliminated by later observers by working in vacuum.) In 1890 they described[3] what was the forerunner of the modern photoelectric cell, *viz.*, a glass bulb containing alkali metals or their alloys or amalgams, which was evacuated and then sealed off from the pumps. An auxiliary electrode served to collect the negative carriers given off by the metal so that when it was given a positive potential by means of an external battery an electric current flowed through the cell when illuminated by visible light. In 1892 they used a photoelectric device as the sensitive element in the first photoelectric photometer, used for measuring the ultra-violet radiation from the sun.[4] In the same year they constructed the first gas-filled cell, containing an alkali metal in the presence of hydrogen at a pressure of 0.33 mm—since this pressure gave the "maximum conduc-

[1] W. Hallwachs, *Ann. d. Phys.*, **33**, 301 (1888).
[2] J. Elster and H. Geitel, *Ann. d. Phys.*, **38**, 40 (1889); **38**, 497 (1889).
[3] J. Elster and H. Geitel, *Ann. d. Phys.*, **41**, 161 (1890); **42**, 564 (1891).
[4] J. Elster and H. Geitel, *Ann. d. Phys.*, **48**, 338 (1892); **48**, 625 (1892).

tivity." They also established the fact that the photoelectric current through such cells was directly proportional to the light intensity over a range of intensity of about 1 to 8. In 1894 the same observers discovered the extremely important result that when certain surfaces, that of sodium-potassium alloy in particular, were illuminated by polarized light at oblique incidence the photoelectric current emitted changed very greatly if the plane of polarization of the light was rotated.[1] This is truly a remarkable list of accomplishments for two observers working with an effect whose fundamental nature was not understood until many years later.

The work of Lenard[2] and J. J. Thomson[3] in 1899 is of the greatest significance in the history of photoelectricity, for they first showed that the negative carriers released by light from metal surfaces were identical with the cathode rays of a Geissler tube, and hence that these *negative carriers were simply electrons*. Lenard further established the very important result that the kinetic energy with which the electrons are released is independent of the intensity of the light while the total number of electrons is directly proportional to it. This result is incomprehensible on the wave theory of light and led Einstein in 1905 to take the next great step which may be said to have opened the modern epoch in photoelectricity. Einstein[4] suggested that, so far as the photoelectric effect was concerned, light could be regarded as being made up of tiny corpuscles, or quanta, each containing an amount of energy equal to $h\nu$, where ν is the frequency of the light and h is the famous constant which Planck had introduced into his theory of radiation 5 years earlier. In the absorption of light it was assumed that the quanta disappeared as such but transferred their energy to electrons within the metal and these then escaped as photoelectrons. Hence, the kinetic energy of an escaping electron should equal the energy of the quantum giving rise to it, minus the work done in passing through the surface. This result is expressed in the famous Einstein equation,

$$E = \tfrac{1}{2}mv^2 = h\nu - p,$$

for the propounding of which Einstein later received the Nobel Prize. One of the chief accomplishments during the past 25 years in photoelectricity has been the accurate verification of Einstein's bold prediction over a range of frequencies varying from that of the shortest γ-ray to frequencies in the near infra-red. It is in this way that the photoelectric effect has played such an important part in revolutionizing our ideas of the nature of radiation.

[1] J. Elster and H. Geitel, *Ann. d. Phys.*, **52**, 433 (1894); **55**, 684 (1895).

[2] P. Lenard, *Wien. Ber.*, **108**, 1649 (1899); *Ann. d. Phys.*, **2**, 359 (1900); *Ann. d Phys.*, **8**, 149 (1902).

[3] J. J. Thomson, *Phil. Mag.*, **48**, 547 (1899).

[4] A. Einstein, *Ann. d. Phys.*, **17**, 132 (1905).

The last decade has witnessed great activity in theoretical and experimental investigation in photoelectricity, the results of which will form the chief subject for discussion in subsequent chapters. On the theoretical side it has been found that the photoelectric effect fits naturally into the new quantum mechanics and many photoelectric problems which could not be handled by older theories have yielded to the powerful methods introduced by recent investigators. On the experimental side we have witnessed a steady improvement in the technique for investigating photoelectric problems, and, what is of still greater "practical" interest, the development of the photoelectric cell as an important commercial tool. Although its possibilities for measuring light intensities were recognized and made use of 40 years ago by Elster and Geitel, it is only recently that the development of highly sensitive cells has made the commercial photoelectric photometer practicable. The combination of the photoelectric cell with the thermionic amplifier has yielded an important light-sensitive tool which has innumerable commercial applications and has made possible the realization of such things as television, talking moving pictures, and the transmission of pictures over telegraph lines. There are but few more interesting developments in all of physics than the growth of the surface photoelectric effect from an obscure physical phenomenon to one of profound theoretical significance, and, finally, to one of surpassing commercial importance.

Although not usually regarded as such until recently, the change of resistance of selenium when illuminated is in reality a photoelectric effect, and because it occurs *within* the substance it is to be recognized as belonging to the photoconductivity group. According to Bidwell[1] this effect was discovered by Willoughby Smith in 1873 and an exhaustive experimental investigation was carried out by Adams and Day[2] in 1876. An enormous literature relating to selenium has grown up, but, until quite recently, no progress whatever had been made in uncovering the really fundamental processes of photoconductivity. During this last decade, Gudden and Pohl and their collaborators began a systematic study of the whole question of photoconductivity, and in a series of remarkable researches succeeded in discovering how, underlying the complicated phenomena frequently observed experimentally, there was a simple photoelectric effect easily interpreted in terms of the quantum theory.

The third type of photoelectric phenomena dates back further than either of the two others, for the first observation was made in 1839 by Becquerel who discovered that the electromotive force of a certain type of voltaic cell changed on illuminating one electrode. It has happened that the subsequent work in this field was carried out largely by physical

[1] S. Bidwell, *Phil. Mag.*, **20**, 178 (1885).
[2] W. G. Adams and R. E. Day, *Phil. Trans. Roy. Soc.*, **167**, 328 (1876).

chemists and the interpretation was generally attempted in terms of chemical processes rather than in terms of a separation of photoelectrons by light. The recently discovered cuprous-oxide-on-copper cell, in which we have essentially a photovoltaic effect, has, however, received a natural and straightforward explanation in terms of movements of photoelectrons. It is possible that some or perhaps all of the other photovoltaic effects could be accounted for in a like manner if some way could be found to separate the secondary effects from the presumed fundamental photoelectric effect.

We shall close this chapter with a list of books or summaries which have been published from time to time on photoelectricity.

ALLEN, H. S.: "Photo-Electricity," 221 pp. (Longmans, Green and Co., 1913).

———: "Photo-Electricity," 2d ed., 320 pp. (Longmans, Green and Co., 1925).

ANDERSON, JOHN S. (editor): "Photoelectric Cells and Their Applications" (published by the Physical and Optical Societies of London, 1930).

BECKER, A.: "Lichtelektrische Wirkung," *Handbuch der Experimentalphysik*, Vol. XXIII, pp. 1041–1544 (1928).

CAMPBELL, N. R., and DOROTHY RITCHIE: "Photoelectric Cells," 209 pp. (Sir Isaac Pitman & Sons, 1929).

GUDDEN, B.: "Lichtelektrischen Erscheinungen," 325 pp. (Julius Springer, 1928).

HALLWACHS, W.: "Die Lichtelektrizität," *Handbuch der Radiologie*, Vol. III, pp. 245–595, (Leipzig Akademische Verlagsgesellschaft, 1916).

HUGHES, A. L.: "Photo-Electricity," 144 pp. (Cambridge University Press, 1913).

———: (transl. by M. Ikle): "Die Lichtelektrizität" (Johann Ambrosius Barth, 1914).

———: "Report on Photo-Electricity," *Nat. Research Council, Bull.*, pp. 83–127, (1921).

LADENBURG, R.: *Jahrbuch der Radioaktivität*, Vol. VI, pp. 428–433 (1909).

POHL, R., and P. PRINGSHEIM: "Die Lichtelektrischen Erscheinungen," 114 pp. (Vieweg, 1913).

v. SCHWEIDLER, E.: *Jahrbuch der Radioaktivität*, Vol. I, pp. 359–366 (1904).

ZWORYKIN, V. K., and E. D. WILSON: "Photocells," 209 pp. (John Wiley & Sons, Inc., 1930).

CHAPTER II

THE FUNDAMENTAL LAWS OF PHOTOELECTRICITY

In investigations on the emission of electricity from matter illuminated by light, the principal variables are the intensity, frequency, and state of polarization of the light, on the one hand; and the number, direction of emission, and the velocity of the photoelectrons, on the other. The problem of the physicist is to find out what relations exist between these two sets of variables and to compare these relations with theory. Among the relations between the characteristics of the light and of the photoelectrons produced, three have outstanding significance because of their simplicity and because of their very direct bearing on theories of radiation. These are: (1) that the photoelectric current is directly proportional to the intensity of the light; (2) that the energy with which the photoelectron is emitted is a linear function of the frequency of the light producing it; and (3) that this energy is independent of the intensity of the light. Results 2 and 3 are significant in that they are easily and naturally interpretable on the quantum theory and in that they are inexplicable on the wave theory. Taking the view of the quantum theory, which regards light as being a torrent of small corpuscles, each containing energy of amount $h\nu$, it is self-evident that, if each quantum releases a photoelectron, then the photoelectric current will be simply proportional to the number of quanta, *i.e.*, directly proportional to the intensity of the light. An equally simple relation follows for the connection between the energy of the photoelectron and the frequency of the light. Einstein[1] postulated that the whole of the energy of the quantum, $h\nu$, disappeared as radiation energy and reappeared as the energy of the photoelectron. If p measures the work which the electron has to do on passing through the illuminated surface (because of the forces tending to keep it within the metal) to the space outside where its kinetic energy $\frac{1}{2}mv^2$ can be measured, then

$$\tfrac{1}{2}mv^2 = h\nu - p. \tag{2-1}$$

This equation—known as Einstein's photoelectric equation—is perhaps the most important single equation in the whole quantum theory, and is the key to a vast number of results outside the restricted domain of photoelectricity, as well as within it. Constant application of Einstein's equation in modern physics has made it so familiar and useful that we are apt to forget how revolutionary it was when it was first proposed. The

[1] A. Einstein, *Ann. d. Phys.*, **17**, 132 (1905); **20**, 199 (1906).

quantum theory was then in its infancy; Planck had recently introduced the notion of discontinuity into the radiation process in order to derive his equation for black-body radiation; but so powerful was the influence of the wave theory that he felt compelled to restrict the idea of discontinuity to the actual processes of emission and absorption, leaving the continuous character of radiation in space unaltered. To make the break with the old wave-theory conceptions still less, he succeeded later in restricting the quantum process to the act of emission only, so that no change from the old view of continuity in absorption was necessary. Einstein, however, took the exceedingly bold step of carrying the idea of discontinuity over from the acts of absorption and emission to the structure of radiation itself, and so obtained his equation. As there was little or no experimental evidence for or against the equation in 1905, this equation is to be regarded as one of the great and successful predictions in physics, comparable with that of Maxwell as to the electromagnetic character of light. Since the energy of the individual photoelectron is determined solely by the energy in the particular quantum which produces it, it is easily seen that an increase in the intensity of the light should lead merely to a proportional increase in the number of photoelectrons emitted, without affecting their individual energies in the least. The picture implied in Einstein's equation is a remarkable one. Sir William Bragg has said: "It is as if one dropped a plank into the sea from a height of 100 ft., and found that the spreading ripple was able, after traveling 1000 miles and becoming infinitesimal in comparison with its original amount, to act on a wooden ship in such a way that a plank of that ship flew out of its place to a height of 100 ft." These experimental results cannot be explained in any natural manner on the basis of the wave theory of light. For example, since the electric force in the wave front must increase when the intensity of the light increases, it is very difficult to understand why the velocity of ejection of the photoelectron should be absolutely unaffected by a change in the intensity of the light. "It is as though the waves beating on a beach were doubled in their height and the powerful new waves disturbed four times as many pebbles as before, but did not displace a single one of them any farther nor agitate it any more violently than the original gentle waves did to the pebbles that they gently washed about."[1]

THE LINEAR RELATION BETWEEN THE ENERGY OF EMISSION AND THE FREQUENCY OF THE LIGHT

2-1. Principles of Measurement and Experimental Methods.—To test the truth of Einstein's equation, it is necessary to measure the energy with which the electrons are emitted from a surface when illuminated by monochromatic light, and to find how this energy alters as the frequency

[1] K. K. Darrow, "Contemporary Physics," p. 121 (D. Van Nostrand Company, Inc., 1926).

of the light is changed. We shall discuss the principles involved in these measurements before taking up specific investigations. Monochromatic light is easily obtained by means of the various monochromatic illuminators now available. When light is allowed to fall on a metal, it is absorbed within a very thin layer, and the production of the photoelectrons occurs within this layer. On account of the different distances which the escaping photoelectrons have to travel through the material before they emerge at the surface, it is evident that, even if they are originally released with one and the same energy, they will emerge with a variety of energies ranging from a maximum (their original energy) down to zero. Those emerging with the greatest energy are, on this view, those which have not suffered energy losses by collision and are obviously the proper ones by which Einstein's equation should be tested.

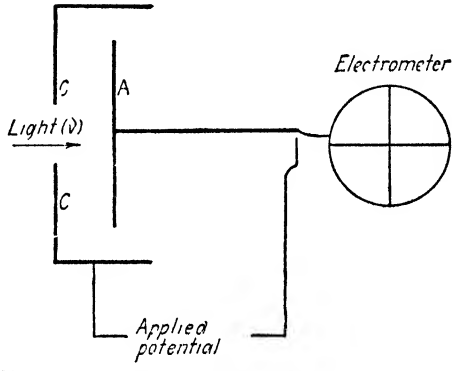

FIG. 2-1.--Typical arrangement for photoelectric investigations.

The velocities of electrons, in general, may be investigated either by an examination of their deflectability in a magnetic field or by a study of their behavior when subjected to different retarding electric fields. In investigations on the velocities of photoelectrons, however, the retarding electric-field method has almost invariably been used. (Ramsauer is apparently the only physicist who has employed magnetic methods for studying velocities of photoelectrons.) Although the forms of the apparatus used by different physicists for investigating velocities of photoelectrons differ widely in size and shape, the way in which they all work may be clearly illustrated by a very simple diagram. In Fig. 2-1, A represents the substance which gives off photoelectrons when illuminated by monochromatic light of frequency ν. The retarding or accelerating field acting on the electrons is produced between A and an electrode C, which more or less surrounds A, and in which it is convenient to have an aperture through which the light passes to illuminate A. To prevent the motion of the photoelectrons being impeded by air molecules, the investigation must be carried out with a vacuum between C and A. When A is illuminated by light of sufficiently short wave-length, it emits a heterogeneous group of electrons whose velocities range from a maximum down to zero. If now a suitable retarding potential of V volts be applied between C and A, photoelectrons whose velocities are less than a certain critical value are not allowed to get to C, while those whose velocities exceed this value are able to get across.

Strictly speaking, the critical velocity which divides the electrons into the two groups changes somewhat with the direction of emission of the photoelectrons, except in the special case where A is a small sphere and C a much larger concentric sphere. For the present, however, we shall ignore the effect of direction of emission and merely assume that all photoelectrons with velocities greater than the critical value get across while those whose velocities are less than this critical value are forced back into A.

The actual retarding field between C and A is not determined merely by the applied potential V. To V must be added (algebraically) the contact difference of potential K between C and A which is always present unless C and A happen to be identical in material and in surface treatment. (C is *electronegative* to A, if the contact difference of potential K is such that it tends to *stop* the passage of electrons from A to C.) The full retarding potential is therefore $V + K$. If a photoelectron emerges from A (and moves in a direction perpendicular to A) with kinetic energy $\frac{1}{2}mv^2$, it will just fail to get to C if its kinetic energy is all used up in overcoming the retarding forces, *i.e.*, if

$$\tfrac{1}{2}mv^2 = (V + K)e = V'e, \tag{2-2}$$

V is frequently termed the *stopping potential.* All electrons with velocities less than v will be turned back to A, while all with velocities greater than v will get across. Thus the current registered by the electrometer will be due solely to these faster electrons, and consequently the current obtained with any given retarding potential is a measure of the number of electrons with energies greater than the energy corresponding to the retarding potential. This equation accounts for the very prevalent and convenient custom of expressing the velocity, or energy, of electrons in terms of *volts* or *electron volts* instead of in centimeters per second or in ergs. An electron is said to have a velocity, or energy, of V' volts, when, in the absence of collisions, it has to fall through a potential difference of V' to reduce its velocity v, and therefore its kinetic energy $\frac{1}{2}mv^2$ to zero. As a result of this practice, it is often convenient to discuss the Einstein equation in the form

$$V'e = h\nu - p \tag{2-3}$$

where V' is the energy of the electron expressed in e.s.u. (= volts/300).

To find the frequency ν_0 for which the photoelectron emerges from the surface with zero energy, we write $V'e = 0$, and $\nu = \nu_0$ in the Einstein equation, and so obtain

$$0 = h\nu_0 - p. \tag{2-4}$$

From this, combined with Eq. (2-3), we get

$$V'e = h\nu - h\nu_0 \tag{2-5}$$

which is an alternative form of the equation. The frequency ν_0 is an important characteristic of the substance, for it is not only that frequency

at which photoelectrons just emerge with zero velocity, but it is also that frequency below which there is no photoelectric effect. Hence the term *threshold frequency.*

2-2. Energy Distribution Curves.—Let us now consider the variations in the photoelectric current obtained from A, by altering step by step the potential V, applied between C and A from a large accelerating value through zero to a suitable retarding value. In general (ignoring secondary effects which have to be avoided by proper design and choice of materials), a curve is obtained which is like that shown in Fig. 2-2. This has the following characteristics. When the applied voltage is accelerating and above a certain small value of the order of 1.0 volt, the photoelectric current reaches a constant value and may therefore be called saturated. To the left of this, that is, for small accelerating potentials and for all retarding potentials, the photoelectric current falls

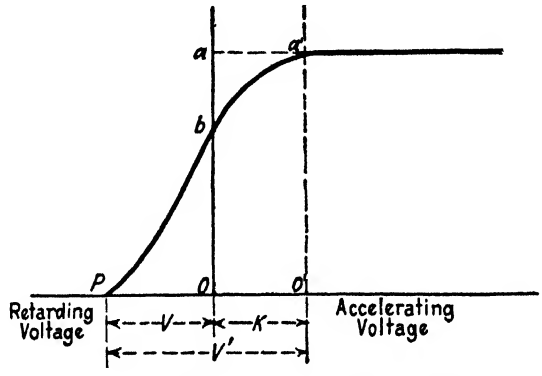

FIG. 2-2.—Typical current voltage curve.

steeply and regularly to zero and cuts the retarding potential axis at a finite angle.[1] If now the curve be discussed solely with reference to the applied potential V (*i.e.*, ignoring altogether the existence of K), the sloping part of the curve to the *right* of the ordinate at zero implies that a certain number of photoelectrons (ab) require a small accelerating potential to pull them out of the metal A, while each ordinate to the *left* of the zero ordinate measures the number of electrons escaping with initial energies equal to and greater than the particular energy associated with that ordinate, and which, of course, is measured in volts by its position on the potential axis. The explanation of the presence of these electrons which apparently require a field to help them out is that they do not really exist. If the contact potential difference K, which is almost always present, is added to V, so as to give the *real* value of the potential

[1] The diagram and discussion refer only to the case when C is electronegative to A. If it were electropositive the curve would become saturated on the left side of the ordinate at the origin.

difference V', actually existing and effective between C and A, then the origin of zero accelerating potential is shifted to O'. The ordinate at this, the correct origin of accelerating potential, now passes through the photoelectric current curve exactly where it starts to deviate downwards from the horizontal part. It is thus seen that when the contact potential difference is properly taken care of, the situation is simplified in that it is no longer necessary to attempt to explain the presence of photoelectrons apparently requiring an accelerating potential to help them out. The fact that the photoelectric current curve begins to drop immediately we cross over from accelerating potentials to retarding potentials simply means that we have photoelectrons whose emission energies range from zero to a maximum value. The energy of the fastest photoelectrons emitted is clearly measured, in volts, by $O'P$. One feature to be noted is that the curve cuts the potential axis at a finite angle and does not approach it asymptotically. This signifies that there is a perfectly definite and clear-cut maximum energy of emission, and that there is nothing resembling the case of the Maxwellian distribution of energy among the electrons emerging from a glowing filament, in which there is, of course, no upper limit to the energies which the electrons may have.

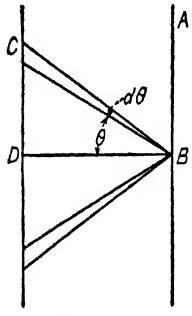

FIG. 2-3.

The actual distribution of energies may be obtained by differentiating the curve Pba'. Clearly, where the curve is steepest, there is the point where there is the maximum number of electrons with energies between V' and $V' + dV'$. The photoelectric current curves obtained in actual experiment are of the type shown in Fig. 2-2, and from this it is to be inferred that the most frequently occurring electron energy is roughly half way between the maximum energy and zero energy. We shall, for the sake of brevity, often refer to the curve Pba' as an energy distribution curve from which the true energy distribution curve is obtained by differentiation. So long as we keep this in mind, no confusion need arise.

The great majority of investigations in which the photoelectric current has been plotted against retarding potentials have been concerned particularly with the determination of the exact position of P. This can be carried out accurately, even though the *shape* of the curve experimentally obtained may not quantitatively reflect the proper distribution of energies. A few investigations by Richardson and his co-workers, to be discussed later, have, however, been carried out to test certain theories bearing on the distribution curve. For such purposes, it is necessary to inquire under what circumstances the curve, given by plotting the photoelectric current against retarding potentials, will lead to a true energy distribution curve. We can easily show that, when C and A are two infi-

nite parallel plates, the photoelectric current curve does not remotely resemble the real energy distribution curve. Suppose that the electrons are emitted equally plentifully in all directions from the point B (Fig. 2-3) in the right-hand plate, and that all start off with one and the same velocity. The actual energy distribution should then be represented by $PQRS$ (Fig. 2-4). The number of electrons emitted between the cones defined by θ and $\theta + d\theta$ is $n_0 \sin \theta \, d\theta$ where n_0 is the total number emitted from B in all directions. Now consider what potential difference between C and A is necessary to stop an electron, when the electron starts off from B: (1) normally, and (2) in a direction making an angle θ with BD. In Case 1 an electron moving with a velocity v cm/sec is just turned back by a potential difference V_0 where V_0 is given by $V_0 e = \frac{1}{2}mv^2$. In Case 2, however, it is only the component of velocity $v \cos \theta$ which is acted on by the opposing field and hence a potential difference $V_0 \cos^2 \theta$ is just sufficient to prevent the electron getting across. The number of electrons which get across in spite of the opposing potential $V_0 \cos^2 \theta$ is the number emitted *within* the cone θ, and this amounts to $n_0 \int_0^\theta \sin \theta \, d\theta = n_0(1 - \cos \theta)$. Writing $V = V_0 \cos^2 \theta$ and $n = n_0(1 - \cos \theta)$, and eliminating $\cos \theta$ we see that the curve representing n as a function of the retarding potential V is a parabola $PTRS$ with its vertex at R. Thus the photoelectric current curve $PTRS$ which would be given by experiment has no resemblance whatever to the true energy-distribution curve $PQRS$. The curve $PTRS$ implies that all energies are present, which is contrary to the assumption made at the beginning that all the electrons possess the same energy V_0. This, therefore, illustrates in a striking manner the necessity for caution in making inferences from such curves. In fact, whether the electrodes are exactly parallel as in the case considered or not, whenever the electron approaches the boundary obliquely it is stopped by a potential less than that corresponding to its energy. It will be noted, however, that the maximum energy given by the experimental curve $PTRS$ coincides with the actual maximum energy. Hence, in investigations in which the interest is focused on the maximum energy of emission, the distortion of the curve from the true distribution curve is of but little importance. To obtain an undistorted distribution curve it is necessary that the electrons reach the electrode C without any appreciable velocity tangential to the surface. This is most directly realized when C is a large hollow sphere, concentric with a much

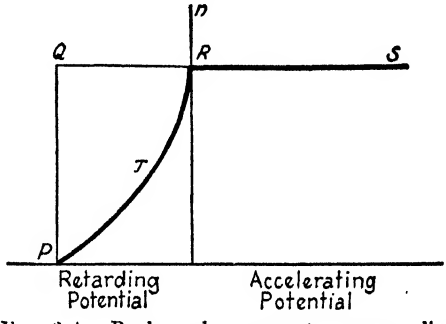

FIG. 2-4.—Real and apparent energy distribution curves.

smaller sphere A, from which the photoelectrons are ejected by suitable illumination.

We have now to consider two other effects whereby the distribution of energy curves may be seriously distorted in actual experiments. The first is that of reflection of electrons. In the foregoing discussion, it has been assumed that the electrons leaving A and reaching C stay there (Fig. 2-1). Suppose now that a fraction of these electrons are reflected back or give rise to secondary electrons leaving C. When the potential of A is negative with respect to C by more than a volt or two, these secondary or reflected electrons are not allowed to return to A, and so there is no distortion of the curve. But when the potential of A is but slightly negative to that of C, and always when it is positive, the effect of the reflection of electrons is always to reduce the ordinate, giving rise to Pbd instead of Pad (Fig. 2-5). It is to be noted that this effect cannot shift the point P which measures the maximum emission energy, although it alters the angle at which the curve cuts the potential axis. It will be noticed that the presence of electrons reflected from C will shift the position of the beginning of saturation from a to d, and so will give an effect somewhat similar to the effect of neglecting the contact potential difference. The two effects are, of course, totally different as to origin. Attempts have been made to diminish the effect of electron reflection by covering C with substances like soot, which reflect electrons comparatively feebly.

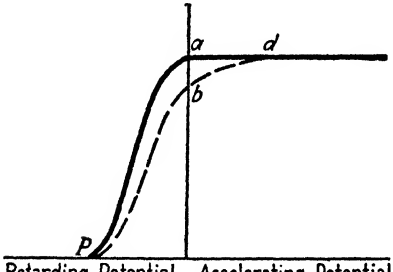

FIG. 2-5.—Distortion due to reflected electrons.

The second effect causing distortion of the distribution of energy curve is present whenever the electrode C is photoelectrically active as well as A. Light falling on A is, in part, unavoidably reflected or scattered to C, which therefore emits photoelectrons. Since an accelerating field for electrons from A is a retarding field for electrons from C, the contribution of C to the measured photoelectric current is represented by the dotted line qpr (a sort of inverted and diminished image of the photoelectric current curve from A); hence it is clear that the measured photoelectric

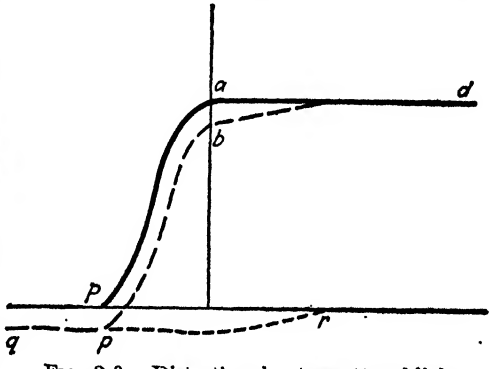

FIG. 2-6.—Distortion due to scattered light.

current will be *qpbd* (Fig. 2-6). It is evident that this effect introduces considerable uncertainty in the determination of P, which gives the maximum emission energy of the electrons from A. This effect can best be avoided by choosing for C a substance which is photoelectrically inactive over the range of wave-lengths for which we are investigating the photoelectric properties of C. This is sometimes, though not always, possible.

2-3. Early Experimental Results.—One of the significant results of Lenard's early work in photoelectricity[1] was that the maximum emission energies of photoelectrons depended on the source of the light. Since direct experiment proved that the intensity was not the determining factor, it was evident that the energies must depend in some way on the wave-length of the light used. Ladenburg[2] was the first to illuminate surfaces with monochromatic light in an attempt to determine exactly what the relationship is. He used surfaces of platinum, copper, and zinc, prepared by mechanical polishing in air after which they were put into the apparatus and the vacuum obtained as soon as possible. To illuminate his surface with different monochromatic radiations he used six different wave-lengths, all between 2000A and 2600A. If V measures the maximum emission energies in volts of the photoelectrons produced by light of wave-length λ, he found that he could express his results in the form $\lambda\sqrt{V} = const.$ This means that the maximum emission energy is proportional to the *square* of the frequency. Joffé,[3] however, pointed out that Ladenburg's results would fit in equally well with the law that the maximum emission energy of the photoelectrons is a *linear* function of the frequency (that is, the Einstein relation). The reason why it is possible to describe the results by two such different laws is, of course, that the range of wave-lengths over which the experiments were carried out is so short that it is impossible to decide definitely whether the points lie on a straight line or on a short length of a parabola at some distance from its vertex. Kunz[4] and Cornelius[5] concluded that their results on sodium-potassium alloy, and on potassium, respectively, were in better accord with the law proposed by Ladenburg than with Einstein's relation. However, Compton[6] did not consider these results to be sufficiently accurate to be decisive.

Several physicists about this time found that very considerable changes in the stopping potentials, used in determining the maximum emission energies of the photoelectrons, could be produced by various treatments of the surfaces investigated. Thus, sputtering the surface

[1] P. Lenard, *Ann. d. Phys.*, **8**, 149 (1902).
[2] E. Ladenburg, *Phys. Zeits.*, **9**, 504 (1907).
[3] A. Joffé, *Ann. d. Phys.*, **24**, 939 (1907).
[4] J. Kunz, *Phys. Rev.*, **29**, 3 (1909); **31**, 536 (1910).
[5] D. W. Cornelius, *Phys. Rev.*, **1**, 16 (1913).
[6] K. T. Compton, *Phys. Rev.*, **1**, 382 (1913).

in vacuum[1] and prolonged illumination[2] of the surfaces by intense ultraviolet light caused the maximum emission energies to increase by amounts of the order 10 to 20 volts. At the time these results were published, it was generally held that the treatment of the surface was in some way effective in removing a retarding surface layer and so allowed the photoelectrons to come through with what was supposed to be their true veloc-

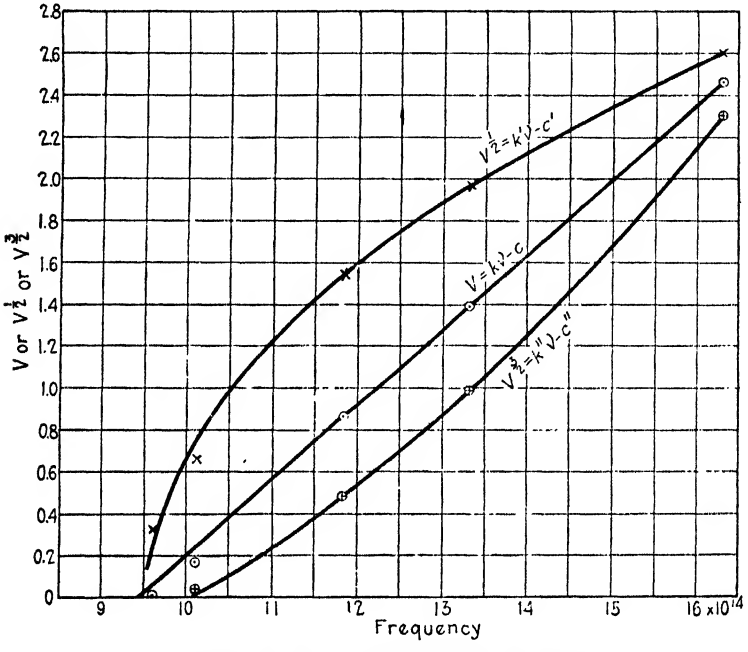

FIG. 2-7.—Test of the Einstein equation. Experimental results fit in with $V = k\nu - p$, but not with $V^{1/2} = k'\nu - p'$, nor with $V^{2/3} = k''\nu - p''$.

ities. (In some of these experiments it is probable that part of the effect, at least, was due to insufficient shielding from electric waves, whose effect will be discussed in Sec. 2-7 of this chapter.) Some experiments by Hughes,[3] however, indicated that passing a discharge through a tube at low pressure, as in the sputtering experiments, had, on the contrary, the effect of building up surface films, which, according to the direction of the discharge, might retard or accelerate the escape of the photoelectrons. In the light of information which became available later,[4] it now appears that abnormally high emission energies are not real and that their apparent existence is to be attributed merely to the formation

[1] O. v. BAEYER and A. GEHRTS, *Verh. d. Deutsch. Phys. Ges.*, **12**, 870 (1910); **13**, 569 (1911).

[2] R. A. MILLIKAN and J. R. WRIGHT, *Phys. Rev.*, **30**, 287 (1910); **34**, 68 (1912).

[3] A. L. HUGHES, *Proc. Camb. Phil. Soc.*, **16**, 167 (1911).

[4] K. T. COMPTON, *Phil. Mag.*, **23**, 579 (1912).

of abnormal contact potential differences within the apparatus. Neglect of the contact potential differences in computing the retarding potentials leads, as we have seen, to erroneous results in calculating the real emission energies, and the error will be proportionally increased when contact potential differences have temporarily abnormally high values.

2-4. Experimental Proof of Einstein's Relation.—The foregoing conflicting results led one of the authors[1] in 1912 to investigate the relation between the emission energies and the frequency of the light. In view of the great and variable effect of the state of the surfaces on the emission energies in previous investigations, the surfaces were all prepared by distillation in vacuum and so were presumably free from contamination. The emission energies were measured immediately afterwards in the same vacuum by the ordinary retarding potential method. On plotting the stopping potentials against the frequency, a straight line was obtained[2] (Fig. 2-7). The results are therefore in accord with the Einstein equation. On the other hand, the results cannot be represented either by the law proposed by Ladenburg, ($V^{\frac{1}{2}} = k'\nu - p'$); or by the one proposed by Lindemann, ($V^{\frac{2}{3}} = k''\cdot\nu - p''$). In view of the importance of the point at issue, the conclusion was confirmed in another way. The maximum emission energies for the three shortest wave-lengths were determined with the greatest possible care. Then taking the stopping potentials V for 1849A and 2537A to determine the constants, the stopping potential for the intermediate wave-length 2257A was computed first for the Einstein relation and then for the Ladenburg relation. It was found that the experimental stopping potential agreed with that calculated on the Einstein relation to within 0.003 volt, but that it disagreed with that calculated on the alternative assumption by 0.083 volt. The Einstein equation also predicts the slope, k of the straight line representing the stopping potential as a function of the frequency. Since $k = h/e$ (Eq. [2-3]), its value should be $300\ (6.55 \times 10^{-27})/(4.774 \times 10^{-10}) = 4.11 \times 10^{-15}$, when V is measured in volts. The experimental values of k for Ca, Mg, Cd, Zn, Pb, Bi, Sb, and As, ranged from 3.17 to 3.79×10^{-15}. The mean value shows a departure of about 13 per cent from the theoretical value.

An important contribution to the study of emission energies of photoelectrons (which appeared simultaneously with the foregoing) was made by Compton, and by Richardson and Compton.[3] In this, ample con-

[1] A. L. Hughes, *Phil. Trans. Roy. Soc.*, **212**, 205 (1912).

[2] The slight departure from the straight line at 2967A and 3126A is accounted for by the fact that the lower velocities of emission were more difficult to determine accurately than the higher velocities. The earth's magnetic field, too, would produce a pronounced curvature of path for the very slow electrons. Hence attention is to be focused on the results for the three shortest wave-lengths.

[3] K. T. Compton, *Phil. Mag.*, **23**, 579 (1912); O. W. Richardson and K. T. Compton, *Phil. Mag.*, **24**, 575 (1912).

firmation of the Einstein linear relation was presented. Moreover, the significant part played by contact potential differences in measurements of emission energies of photoelectrons was pointed out for the first time, and the interpretation of results was thereby much simplified. The illuminated substance consisted of a strip of metal about 5 mm^2 in area, which was surrounded by a concentric bulb of glass of diameter 7.5 cm, and silvered on the inside. This particular arrangement of electrodes approximates very closely to that of a large sphere surrounding a much smaller one from which the photoelectrons emerge. We saw in Sec. **2-2** that such an arrangement, in contrast to most arrangements of electrodes, gives undistorted energy distribution curves. The various energy distribution curves for photoelectrons from aluminum, when illuminated by light of various wave-lengths, are shown in Fig. 2-8. These results illustrate very clearly the part played by contact potential differences which has already been touched upon in Sec. **2-1.** When the electron currents (from Al) passing across the apparatus against various retarding (and accelerating) potentials are plotted, the curves do not attain their saturation values until an accelerating potential of as much as 1.3 volts is applied. On shifting the ordinate by the amount of the measured contact potential difference, it was found that the corrected zero ordinate passed through the distribution curves just at that point where the curves flatten out. Thus the photoelectrons emerge with energies ranging from zero to a maximum, and there are no electrons which apparently require a small accelerating potential to drag them out. On plotting the corrected retarding potentials against the frequency of the light, the straight line in Fig. 2-9 is obtained. (The lower line is the plot obtained when the applied potential, uncorrected for contact potential difference, is used.) This investigation of Richardson and Compton and that of the author[1] were the first to show definitely that the maximum emission energy of photoelectrons is a linear function of the frequency—the now familiar Einstein relation. In contradistinction with previous

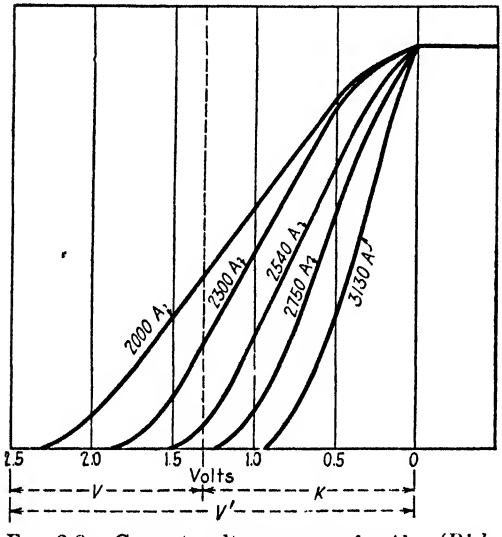

FIG. 2-8.—Current voltage curves for Al. (*Richardson and Compton.*)

[1] A. L. HUGHES, *Phil. Trans. Roy. Soc.*, **212**, 205 (1912).

results they discriminate decisively against the suggested alternative relations: $\sqrt{V} = k'\nu - p'$ (Ladenburg), and $V^{\frac{2}{3}} = k''\nu - p''$ (Lindemann).

The values of k for the various metals studied by Richardson and Compton were grouped around 3.3×10^{-15}, which is about 20 per cent below the theoretical value.

To Millikan and his associates we are indebted for a remarkably accurate and extensive study of the photoelectric effect in its relation to the Einstein equation. All possible sources of error were carefully examined and the investigations were then carried out so as to diminish

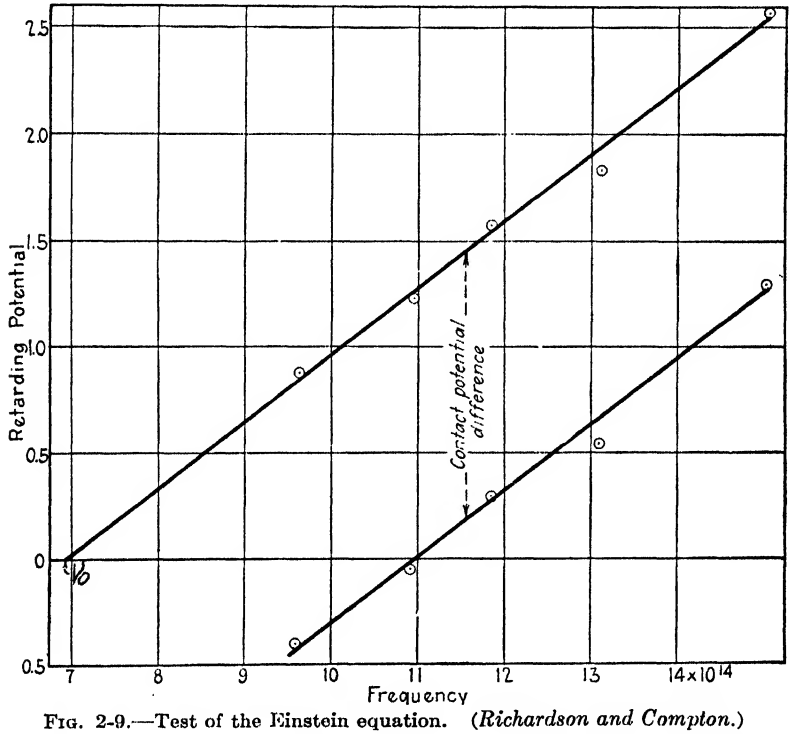

FIG. 2-9.—Test of the Einstein equation. (*Richardson and Compton.*)

their effect to the utmost. The strict linear relationship implied in the Einstein equation was once again verified. Moreover, for the first time, the slope of the line connecting the maximum emission energy with the frequency turned out to be accurately h/e. In fact this agreement with the predicted value, combined with a critical examination of the sources of error in this investigation, fully justifies Millikan in regarding his results as affording an alternative determination of h accurate to 0.5 per cent.[1] The part played by contact-potential differences was investigated with extreme thoroughness. The essential features of Millikan's apparatus are shown in Fig. 2-10. That used by Kadesch[2] was very

[1] R. A. MILLIKAN, *Phys. Rev.*, **7**, 362 (1916).

[2] W. H. KADESCH, *Phys. Rev.*, **3**, 367 (1914).

much the same, except for the omission of the device S for measuring the contact potential difference. Cast cylinders of sodium, lithium, and potassium were mounted on a wheel so that each, in turn, could be brought: (1) in front of the Faraday cylinder C for the photoelectric investigation; (2) in front of the plate S for measuring the contact potential difference between it and the metal under investigation; and (3) into position so that the knife P could shave off a thin layer to expose a new surface. The last feature, which has been called a "machine shop in a vacuum," is an exceedingly important device, for it permitted the renewal of the surfaces of these easily contaminated metals at will. Although these alkali metals are difficult to handle, they possess a great advantage in that they are photoelectrically active over a much larger portion of the accessible spectrum than are other metals. Sodium, as prepared in Millikan's experiments, was photoelectrically active to as far as 6800A. This allows a study of the emission energies over a much larger range of wave-lengths than is possible with other metals, thus permitting a decided advance in precision. Light falling on the exposed surface of the alkali metal is, in part, reflected to the inside of the Faraday cylinder. If the Faraday cylinder is photoelectrically active, it emits photoelectrons, and so introduces an uncertainty in the determination of the exact value of the retarding potential, necessary to stop the fastest electrons from the surface studied (see Sec. 2-2). Millikan completely avoided this source of trouble by making the Faraday cylinder of oxidized copper whose photoelectric threshold was 2688A and restricting almost all his measurements to tests with light of longer wave-length than this. Care was also taken to guard against stray light passing through the monochromatic illuminator along with the light which the instrument was set to transmit. The light was obtained from a quartz mercury arc lamp and the wave-lengths selected for illuminating the surfaces were 5461, 4339, 4047, 3650, 3125, 2535, and 2399. The photoelectric currents for the different wave-lengths plotted against the applied potentials are shown in Fig. 2-11. The freshly exposed alkali-metal surfaces give very large photoelectric currents and it is consequently possible to make precise determinations of where the curves plunge into the potential axis. It will be noticed that these curves all

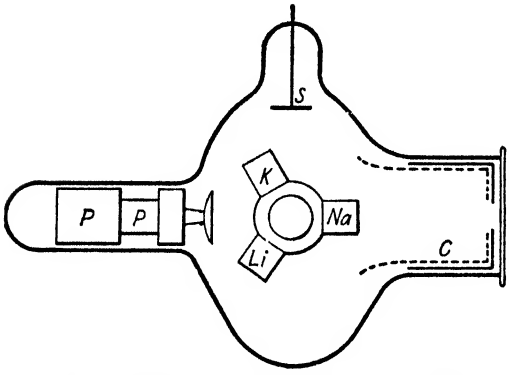

FIG. 2-10.—Millikan's apparatus for the study of emission energies of photoelectrons.

intersect the potential axis at finite angles, indicating most clearly the presence of definite maximum energies. There is no suggestion of an asymptotic approach. The contact potential difference between the Faraday cylinder and the alkali metal was determined by turning it until it was in front of S, which was of exactly the same oxidized copper as the Faraday cylinder. When there is an electrostatic field between S

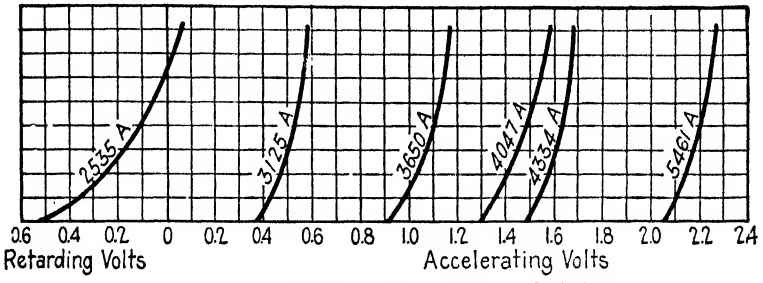

FIG. 2-11.—Current-voltage curves. (*Millikan.*)

and the metal in front of it, arising, for example, from the contact potential difference, a small displacement of S causes an inductive electrostatic effect to be recorded on the electrometer connected to one or the other electrode. The contact potential difference is found by measuring that compensating potential which must be applied between S and the alkali metal to give no inductive effect on moving S. On plotting the stopping

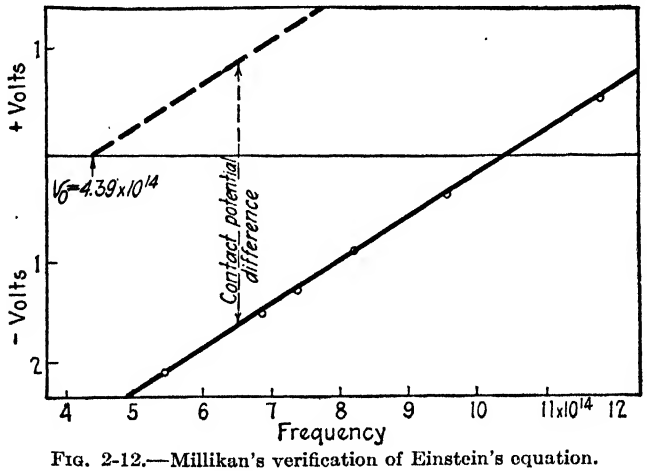

FIG. 2-12.—Millikan's verification of Einstein's equation.

potentials for sodium from Fig. 2-11, against the frequency of the light used, the lower straight line in Fig. 2-12 was obtained. On correcting for contact difference of potential, the line was displaced parallel to itself as shown, cutting the horizontal axis at the threshold frequency, $\nu_0 = 43.9 \times 10^{13}$, which is equivalent to a wave-length 6800A. Almost identical results were obtained in experiments on lithium and in other

experiments on sodium. From the slope of such lines Millikan finally concluded that the most probable value for h is 6.57×10^{-27}, with a probable error of less than 0.5 per cent.

Kadesch[1] had obtained values of 6.16×10^{-27} and 6.09×10^{-27} for sodium and potassium, respectively, in an earlier investigation. Kadesch and Hennings[2] obtained 6.45×10^{-27} and 6.41×10^{-27} for magnesium and aluminum, respectively. These results are not so accurate as those of Millikan, but they do show that the slope of the line is, within experimental error, that given by Einstein's relation.

2-5. Contact Difference of Potential in Photoelectric Experiments.—Millikan[3] has made a detailed study of the relations between the contact potential differences between metals, their stopping potentials and their photoelectric thresholds, and has drawn important conclusions from this study. Let A (Fig. 2-1) be a metal surface which emits photoelectrons when illuminated by light of frequency ν, and whose photoelectric threshold is ν_0. Let V be the potential difference which has to be applied in order to stop the fastest electrons. The actual potential difference existing between C and A must include the contact potential difference K. The Einstein relation becomes

$$(V + K)e = h\nu - h\nu_0. \tag{2-7}$$

Now substitute another surface B in place of A, for which the stopping potential, the photoelectric threshold, and the contact potential difference relative to C are respectively V', ν_0' and K'. The following equation then holds

$$(V' + K')e = h\nu - h\nu_0'. \tag{2-8}$$

Subtracting Eq. (2-7) from Eq. (2-8), we get

$$(K' - K) = \frac{h}{e}(\nu_0 - \nu_0') - (V - V'), \tag{2-9}$$

which may be expressed in words as follows:

$$\begin{pmatrix}\text{Contact potential}\\ \text{between } A \text{ and } B\end{pmatrix} = \frac{h}{e}\begin{pmatrix}\text{frequency diff.}\\ \text{of thresholds}\end{pmatrix} - \begin{pmatrix}\text{difference between}\\ \text{stopping potentials}\end{pmatrix}.$$

Many experiments made by Millikan, and also by Hennings and Kadesch, show that when any two clean metals (A and B) are brought in rapid succession before a Faraday cylinder C, their stopping potentials V and V' for photoelectrons ejected by light of the same frequency are identical. Hence Eq. (2-9) takes the simpler form

$$K' - K = \frac{h}{e}(\nu_0 - \nu_0'), \tag{2-10}$$

which states that the contact potential difference between any two metals

[1] W. H. Kadesch, *Phys. Rev.*, **3**, 367 (1914).

[2] W. H. Kadesch and A. E. Hennings, *Phys. Rev.*, **8**, 221 (1916).

[3] R. A. Millikan, *Phys. Rev.*, **7**, 18, 355 (1916); **18**, 236 (1921); "The Electron," p. 253, 2d ed. (The University of Chicago Press, 1924).

A and B is merely equal to h/e times the difference between their thresholds. (Equation [2-10] had already been discussed by Richardson and Compton in connection with their results.) Under certain circumstances, as for example, when one of the surfaces, say A, is oxidized copper and the other, B, is lithium, it was found that Eq. (2-9) held, but *not* Eq. (2-10). The contact difference of potential between them was 1.52 volts, while h/e times the frequency difference between their thresholds was 2.53 volts and the difference between the stopping potentials was 1.00 volt. Inserting these in Eq. (2-9), we get

$$1.52 = 2.53 - 1.00,$$

which shows that, within the limits of experimental error, Eq. (2-9) is satisfied. Some months later the values changed to

$$1.11 = 2.42 - 1.13.$$

Possibly the best way of visualizing what happens is as follows. Let us consider that initially both surfaces A and B are "clean," and that Eq. (2-10) is satisfied. Now suppose that, in some way or another, a layer of negative electricity builds up on *one* of the surfaces. (To make the picture more concrete, one could perhaps imagine a very thin layer of grease, or other non-conductor, over the metal surface, such that some of the electrons moving towards the metal are caught on the outer surface of this non-conductor and thus prevented from entering into the body of the metal. Owing to the presence of the negative charge thus entangled over the surface, the metal will act in respect to its surroundings as though it had a more negative potential than it would have in the absence of the postulated non-conducting film.) This will change the measured contact potential difference $K' - K$, but will have no effect on the photoelectric thresholds, for these are determined by noting the minimum frequency of the light which calls out a photoelectric effect. Consequently, if Eq. (2-10) held before, it cannot hold now. Anything of the nature which we have pictured will change the left side of Eq. (2-9) through $K' - K$, and the right side through $V - V'$ by the same amount, and so it is evident why the equation will always hold, as Millikan found was the case.[1] Millikan regards pairs of metals, whose behavior is represented by Eq. (2-10), as having *intrinsic* or *true*, contact potential differences, while pairs of metals whose behavior can only be represented by the more comprehensive Eq. (2-9) are said to show "spurious" contact potential differences. In the latter case, it is to be presumed that a charged layer of some kind forms on one (or both) surfaces under such conditions that it cannot disappear in the normal fashion

[1] It is implied in the statement in the text which is equivalent to one in Millikan's paper (*Phys. Rev.*, **18**, 239 [1921]), that the thresholds do not alter. In the numerical illustrations cited, it will be observed that there is a change in the values of the threshold, which is, however, small compared with the almost equal changes in the $K' - K$ and $V - V'$.

into the interior of the metal. The slow formation or disappearance of such charges can be followed by checking Eq. (2-9) from time to time and noting the gradual changes in the numerical values of the quantities involved. As a matter of record, Millikan found that these spurious contact potential differences appeared only when one of the pair of surfaces was oxidized copper. Presumably, then, it was at this surface that the spurious contact potential difference originated. Whenever pairs of clean metals were studied, Eq. (2-10) was found to hold, and conversely when it holds, we may infer the absence of spurious contact potential differences.[1]

Mention should be made of an investigation by Ramsauer[2] on the emission energies of photoelectrons. The novel feature of this method was that the velocities of the photoelectrons were measured by their deflectability in a magnetic field. Ramsauer concluded that there were no sharply defined maximum emission energies for photoelectrons excited by monochromatic radiation. The magnetic-deflection method has the disadvantage that it allows to pass through the slit system only those electrons whose velocities have a specified value, and, moreover, it selects these photoelectrons from among those which are emitted within a very narrow solid angle. Hence, to get measurable electron currents to the collecting cylinder, the slits must be opened to such a point as to impair seriously the resolving power. It appears that this is the reason why Ramsauer failed to find definite maximum emission velocities.[3]

2-6. Recent Tests of Einstein's Equation.—Lukirsky and Prilezaev[4] made a remarkably careful investigation of the emission velocities of photoelectrons from Al, Zn, Sn, Ni, Ag, Cd, Pb, Cu, and Pt. A small sphere of metal under investigation was mounted at the center of a much larger spherical flask which was silver lined. Such an arrangement gives undistorted velocity-distribution curves (Sec. **2-2**). Although scattered light produced a photoelectric effect at the silver surface, and so gave a "reverse" current (Fig. 2–6, Sec. **2-2**), it was possible to determine exactly the value of the stopping potential for the photoelectrons emitted from the inner sphere. In Fig. 2-13 a typical current potential curve is reproduced. Curve 2 is obtained when only the silver lining is illuminated. Curve 1 is obtained when the inner sphere is illuminated directly, so that scattered light also falls on the silver lining. The voltage, at which curve 2 falls to zero, *viz.*, Q, may be assumed to be also the voltage at which the "foot" of curve 1 would become zero. Because the foot of curve 1 is so nearly straight and so can be extrapolated to its zero, it is easy to determine exactly the stopping potential V_{max} for the photoelectrons from the inner sphere. The corrected current voltage

[1] Glasoe (*Phys. Rev.*, **38**, 1490 [1931]) has shown that Eq (2-10) holds very accurately for clean surfaces of Ni and Fe. This is the first time that the equation has been verified with thoroughly outgassed surfaces.

[2] C. Ramsauer, *Ann. d. Phys.*, **45**, 961, 1121 (1914).

[3] R. A. Millikan, *Phys. Rev.*, **7**, 18, (1916); O. Klemperer, *Zeits. f. Phys.*, **16**, 280 (1923).

[4] P. Lukirsky and S. Prilezaev, *Zeits. f. Phys.*, **49**, 236 (1928).

curve (curve 3, Fig. 2-13) is obtained by subtracting the extrapolated "foot" from the experimental curve. In general the foot is relatively much smaller than that shown in Fig. 2-13, which was obtained when the inner sphere was of Pb and gave unusually small photoelectric currents. The values of V_{max} were determined for various wave-lengths of the monochromatic light, from which all stray light of shorter wave-length was removed. Then, as in the preceding investigation, h was computed from the slope of the line giving V_{max} as a function of the fre-

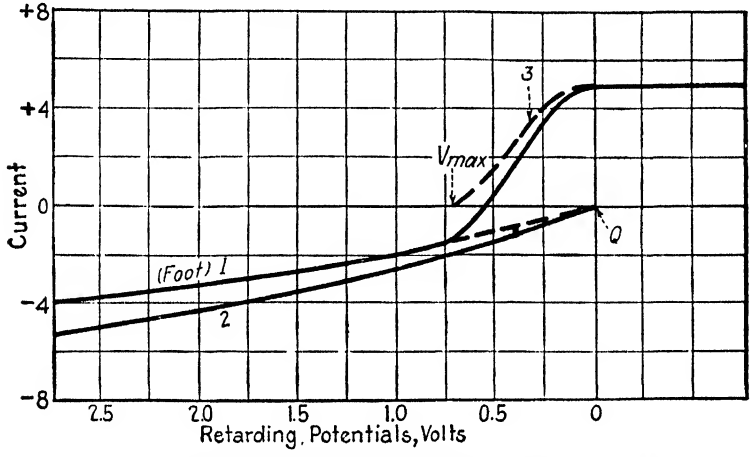

FIG. 2-13.—Current-voltage curve for Pb (retarding potentials have been corrected for contact difference of potential).

quency. The final value was given as 6.543×10^{-27} with a probable error of 0.1 to 0.2 per cent. Equation (2-10) was found to hold within the limits of experimental error.

A very accurate photoelectric determination of h was made by Olpin[1] recently. At one end of the experimental tube he prepared the surface to be illuminated, *viz.*, Na sensitized by S. This was photoelectrically active to beyond 8000A. At the other end of the tube was a cylindrical anode of Ni, coated with soot, which was insensitive to wave-lengths longer than 3500A. By inverting the tube it was possible to slip the sensitized surface into a position where it was surrounded by the anode. While in this position, the measurements of the stopping potentials were made. As the threshold of the anode was well in the ultra-violet, it was possible to determine the stopping potentials for the photoelectrons from the sensitive surface over the extraordinarily wide range of 3500A to 8000A, without having to consider the "reverse" current (Fig. 2-6, Sec. 2-2). Great care was taken to avoid stray light of shorter wave-length than that which the monochromatic illuminator was set to trans-

[1] A. R. OLPIN, *Phys. Rev.*, **36**, 251 (1930).

mit. Olpin considers that his value of h, *viz.*, 6.541×10^{-27}, is "correct to at least three significant figures."

The precision determinations of h by the photoelectric method may be summarized as follows:

TABLE 2-1.—PHOTOELECTRIC DETERMINATIONS OF h

Author	h, erg-sec.	Accuracy claimed, per cent
Millikan (1916)	6.57×10^{-27}	± 0.5
Lukirsky and Prilezaev (1928)	6.543×10^{-27}	± 0.1 to 0.2
Olpin (1930)	6.541×10^{-27}	± 0.15
Birge (1929)	6.547×10^{-27}	± 0.12

The value of h, estimated by Birge[1] from a critical examination of *all* the methods used for its determination, is given for comparison. It appears that the most probable value of h, as determined photoelectrically, is 6.542×10^{-27}, with an error of not more than about 0.15 per cent. The results shown in Table 2-1 are represented graphically in Fig. 2-14.

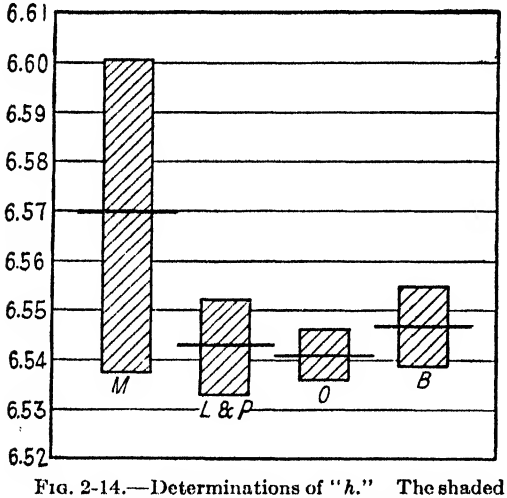

FIG. 2-14.—Determinations of "h." The shaded areas represent the possible inaccuracies as estimated by the authors M(Millikan), L and P (Lukirsky and Prilezaev), O(Olpin), B(Birge).

EFFECTS RELATED TO LIGHT INTENSITY

2-7. The Velocity of Photoelectrons Is Independent of the Intensity of the Light.—On the wave theory, the intensity of the light is determined by the amplitude of the waves, while on the corpuscular theory it measures merely the number of corpuscles flying through a given area. Thus, on the corpuscular theory, one would expect an increase in the intensity of the light to produce only a proportional increase in the number of photoelectrons without changing their energies, since these are presumably controlled by the characteristics of the individual corpuscles. On the wave theory, one might well be prepared to expect a change in the energies of the photoelectrons when the intensity is altered, for we must now

[1] R. T. BIRGE. *Phys. Rev., Supplement*, **1**, 1 (1929).

suppose that the release of the photoelectron is effected by the direct action of the electric force in the light beam. It would appear reasonable to surmise that, when a change of intensity results from a change in the amplitude of the electric force in the light beam, the energy of expulsion of the photoelectron would also change in the same sense, though, to be sure, special systems have been devised where this would not necessarily follow. (In such systems the electric force plays a part somewhat analogous to a trigger releasing a certain store of energy explosively, the force acting on the trigger having nothing to do with the amount of energy released.) To summarize briefly, we may say that, on the corpuscular theory of light, the energy of the photoelectron must be absolutely independent of the intensity of the light; while, on the wave theory, it is highly probable that the energy of the photoelectron depends on the intensity of the light, the exact relationship depending upon the particular model chosen to represent the interaction.

We shall now consider the experimental evidence available. The first investigator to show that the energy of emission of the photoelectron is independent of the intensity of the light was Lenard,[1] who found that a seventy fold change in the intensity of the light did not alter the maximum energy of emission of the photoelectron by as much as 1 per cent. Further direct evidence, confirming this result, was obtained by Ladenburg,[2] Millikan and Winchester,[3] Mohlin,[4] Wright,[5] and Kunz.[6] Perhaps the most striking evidence in support of this relation is a result which, curiously enough, was at first taken to indicate a breakdown of the relation. Millikan[7] had found that, when he used light of identical wavelength from a mercury arc and from an intense spark, to eject photoelectrons from a plate in vacuum, higher retarding potentials were required to stop the photoelectrons produced by the spark. The first inference was that photoelectrons ejected by the intense light of the spark had greater energies than those ejected by the weaker light from the arc. This result was soon found to be incorrect.[8] On taking extremely rigorous precautions to shield the photoelectric cell, the electrometer, and all connecting wires from electric waves by completely enclosing them within a box of metal, then, and only then, was the retarding potential necessary to stop the photoelectron independent of the intensity of the light. The effects obtained without shielding are attributed to the fact that the

[1] P. Lenard, *Ann. d. Phys.* **8**, 149 (1902).
[2] E. Ladenburg, *Verh. d. Deutsch. Phys. Ges.*, **9**, 504 (1907).
[3] R. A. Millikan and G. Winchester, *Phil. Mag.*, **14**, 188 (1907).
[4] Mohlin, *Akad. Abhandl., Upsala* (1907).
[5] J. R. Wright, *Phys. Rev.*, **33**, 43 (1911).
[6] J. Kunz, *Phys. Rev.*, **29**, 212 (1909).
[7] R. A. Millikan, *Phys. Rev.*, **34**, 68 (1912); **35**, 74 (1912); **1**, 73 (1913).
[8] R. Pohl and P. Pringsheim, *Verh. d. Deutsch. Phys. Ges.*, **15**, 974 (1912); R. A. Millikan, *Phys. Rev.*, **1**, 73 (1913).

sparks emit not only light, but also electric waves simultaneously. These waves, passing over the photoelectric cell and connecting wires, set up transient potential differences which, while contributing powerfully to the actual applied potentials during the interval the photoelectrons are moving across the space, leave no record on the voltmeters used to measure the applied potentials. Hence, when these conditions hold, it is impossible to infer what are the actual potentials acting on the photoelectrons; they are certainly different from the steady values given by the measuring instrument. Once having established that light from a mercury arc produces electrons having the same speed as those produced by light from an intense spark, when the same wave-lengths are used, the result may be used as a powerful argument to support the conclusion that the intensity of the light has no effect on the energy of the photoelectrons. The spark gives out its light intermittently, the short periods of intense illumination being separated by (relatively) much longer intervals of no illumination. If it be assumed that the mean intensities of the two sources are of the same order, then the actual intensity of the spark during the periods of illumination must have been very much greater than the intensity of the arc. We therefore conclude that the energies of the photoelectrons are quite independent of the intensity of the light.

Very strong indirect support for the conclusion that the intensity of the light has no effect on the energies of the photoelectrons may be drawn from the results already discussed, establishing the linear relationship between the maximum emission energy and the frequency of the light. Although the intensities of the various strong lines in the mercury-arc spectrum selected for illuminating the metallic surfaces differed widely and irregularly from each other, it is significant that the linear relation was obtained without taking this fact into account. The only inference which can possibly be made is that the energy of the photoelectrons is absolutely independent of the intensity of the light. If it were not so, some sort of a reduction to a common intensity would have to be made before starting to test the linear relation, as it is absurd to suppose that the irregular distribution of intensities among the successive mercury lines just happens not to interfere with the relation between the energy and the frequency.

2-8. Proportionality between the Photoelectric Current and the Intensity of the Light.—One of the first quantitative results obtained in photoelectricity was that of Elster and Geitel,[1] who found that the photoelectric current from potassium in vacuum was proportional to the intensity of the light for small ranges of intensity. This was a very significant result, and its fundamental bearing is the reason why the point at issue has been examined so many times since. The Einstein view of the photoelectric effect demands the release of a photoelectron for every quantum absorbed, and hence the number of photoelectrons escaping—a constant fraction of the photoelectrons released within the surface layers—must be directly proportional to the total number of quanta, *i.e.*, to the intensity

[1] J. Elster and H. Geitel, *Ann. d. Phys.*, **48**, 627 (1893).

of the light. The wave theory, on the other hand, leads to no such unequivocal conclusion. Indeed, one cannot predict the result to be expected on the wave theory unless one considers a particular model which describes precisely the manner in which the photoelectron is broken loose from its moorings. Thus it is conceivable (though certainly not obvious) that the number of photoelectrons released might be more nearly proportional to the amplitude of the electric force in the light beam than to the square of amplitude which measures the intensity. It is also possible, on the same view, that when the intensity of the light drops below a certain value, the electric force in the wave front is insufficient to break the bonds holding the electron to its equilibrium position, indicating a kind of a photoelectric "threshold" in intensity. (The property of the photographic plate whereby no developable image is produced by light of less than a small, but finite, intensity, obviously suggests the possibility of a parallel result in photoelectricity.) The conclusion to which the most reliable experiments all lead is that the photoelectric current is accurately proportional to the intensity of the light. Moreover, there is not the slightest trace of any evidence for any deviation from this relation, either for the weakest light that can be used (so weak that the eye cannot detect it) or for the strongest light available (sunlight). Though practically all investigators acquiesce in regarding this strict proportionality as fundamentally true, it requires most carefully designed photoelectric cells to avoid spurious results which at first sight imply that the law is only approximately true.

Among the earlier investigations on this relation are those of Elster and Geitel,[1] Lenard,[2] Ladenburg,[3] and Richtmyer,[4] who concluded that within the limits of accuracy of their experiments, proportionality between the photoelectric current and the intensity of the light held. As the unresolved light from a source was used, care had to be taken to diminish the intensity by some method which affected all wave-lengths equally. A satisfactory method, adopted by several of the investigators cited, was to move the source known distances from the photoelectric cell and to compute the intensity by the inverse square law. (By reducing his light intensity enormously through reflection from a sooted surface, Lenard[2] showed that the photoelectric current still varied inversely as the squares of the distances from the source, over a range of intensity from 1 to 10^6.) The order of accuracy attained may be illustrated from the work of Richtmyer, who found that the quotient (*photoelectric current/intensity*) varied from 0.29 to 0.26, as the illumination changed from 30 to 600 candle meters.

[1] J. Elster and H. Geitel, *Ann. d. Phys.*, **48**, 627 (1893).
[2] P. Lenard, *Ann. d. Phys.*, **8**, 149 (1902).
[3] E. Ladenburg, *Ann. d. Phys.*, **12**, 573 (1903).
[4] F. K. Richtmyer, *Phys. Rev.*, **29**, 71, 404 (1909).

Photoelectric cells, used in investigations of the relation under discussion, have been of two kinds: the gas-filled, and the vacuum type. The gas in the gas-filled cells is usually argon or helium at such a pressure as to give the biggest magnification of the original photoelectric current through ionization by collision. As such cells are often used for precise photometric work, or are wanted for producing an electric current exactly proportional to the light intensity, it is clearly necessary to know how exact the proportionality between the current and the intensity in the particular cell used really is. If a departure from exact proportionality is recorded, it may well be connected with a lack of constancy of the magnification factor due to ionization by collision, and not with a real lack of proportionality between the number of photoelectrons released and the intensity of the light. Even when conditions are simplified by working in vacuum, a departure from proportionality is generally observed unless special care is taken in designing the cell. Two extreme types of cell are shown in Figs. 2-15 and 2-16. In Fig. 2-15, there are large surfaces of glass on which photoelectrons can collect. This produces a distortion in the electric field, which in turn affects the photoelectric current, and the degree of distortion must depend on the rate at which the surface is being charged, the recent history of the cell, and other factors difficult to specify in quantitative terms. Under such conditions, strict proportionality can hardly be expected. These complications can be avoided, or much diminished, by making the cell as in Fig. 2-16, in which the glass bulb is almost completely lined with a layer of metal, thus diminishing to a minimum the amount of exposed glass on which charges can accumulate. Moreover, this type of cell traps almost completely the light entering and so forms a sort of photoelectric *Hohlraum*, while the other absorbs but a very small fraction of the incident light.

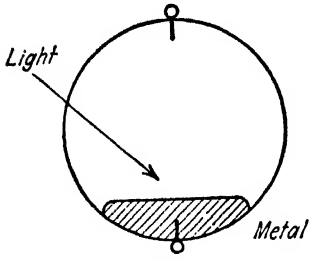

FIG. 2-15.

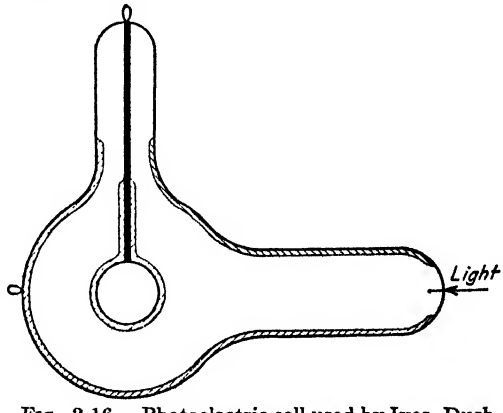

FIG. 2-16.—Photoelectric cell used by Ives, Dushman, and Karrer. Shaded portion indicates alkali metal.

We may regard experiments in this field as being carried out with two distinct purposes in view. The first is to test the accuracy of the proportionality between the photoelectric current and the intensity of the light

as a general law in photoelectricity, while the second is to test whether or not a particular cell is a useful and dependable tool for giving a photoelectric current accurately proportional to the light intensity.

Using carefully designed cells to avoid charges collecting on exposed insulating walls, Elster and Geitel[1] found a strict proportionality between the photoelectric current and the intensity of the light over a very wide range, from 30,000 lux to 6×10^{-4} lux.[2] The cells were generally gas filled (argon at a pressure of less than 1 mm). However, to establish strict proportionality for very intense illumination, they used a completely evacuated potassium cell, because the magnification due to ionization by collision ceased to remain constant when the currents became very large. Later, they showed that strict proportionality still held when the intensities were as small as 3×10^{-9} erg/sec cm^2 for blue light, and 2×10^{-7} erg/sec cm^2 for red light. The former value is lower than the threshold value for the eye.[3] Proportionality still obtains when the sensitive surface is a "thin film" of metal of the order of atomic thickness.[4]

A very thorough examination of the relation between the photoelectric current and the intensity of the light was made by Ives[5] and by Ives, Dushman, and Karrer.[6] Constancy of the ratio was secured only after the cells were carefully designed so as to avoid the building up of negative charges on insulating surfaces within the cell. The type of cell which was finally found to give a strict proportionality is shown in Fig. 2-16, in which both the central electrode and the inside of the bulb are covered with distilled potassium. Proportionality was found to hold, no matter whether the cathode emitting the photoelectrons was the small central cathode or the metallic lining of the bulb. These investigators point out that, if it is desired to use a photoelectric cell for photometric work, it is altogether too risky to assume as a general rule applicable to all cells, that the photoelectric current is directly proportional to the intensity of the light. The characteristics of the particular cell must be investigated. This contention is significantly justified by some later publications. Steinke,[7] using an argon-filled potassium cell of modern manufacture, found a very serious departure from the proportionality law, especially when the applied potentials were close to the discharge potentials. On the other hand, v. Halban and Ebert[8] tested five different cells of the same general type as Steinke's and found a remarkably high degree of proportionality

[1] J. Elster and H. Geitel, *Phys. Zeits.*, **14**, 741 (1913); **15**, 610 (1914).

[2] One *lux* = 1 candle meter; 30,000 lux is about equal to one-third of sunlight.

[3] J. Elster and H. Geitel, *Phys. Zeits.*, **17**, 268 (1916).

[4] H. Geitel, *Ann. d. Phys.*, **67**, 420 (1922); H. E. Ives and A. R. Olpin, *Phys. Rev.*, **34**, 117 (1929).

[5] H. E. Ives, *Astrophys. Jour.*, **39**, 428 (1914); **40**, 182 (1914); **46**, 241 (1917).

[6] H. E. Ives, S. Dushman, and E. Karrer, *Astrophys. Jour.*, **43**, 9 (1916).

[7] E. Steinke, *Zeits. f. Phys.*, **11**, 225 (1922).

[8] H. v. Halban and L. Ebert, *Zeits. f. Phys.*, **14**, 183 (1923).

to hold for all. Kunz and Stebbins,[1] and Kunz[2] found proportionality to hold for neon-filled rubidium cells and for other cells.

Campbell,[3] however, found that it was impossible to make photoelectric cells which did not show some slight departure from strict proportionality. He obtained a closer approximation to strict proportionality when the cathode was a central plate covered with potassium than when it was the potassium lining the bulb (*cf.* Fig. 2-16). This he attributes to the formation of an invisible, but photoelectrically active, film over the window. This film is probably in imperfect electrical contact with the metallic lining, and so, when the lining is the cathode, disturbances are to be expected.

It is evident from the results presented that cells showing departures from proportionality are about as plentiful as those which show strict proportionality. Yet no one seriously questions the view that, fundamentally, there is a strict proportionality between the number of photoelectrons released from the surface and the intensity of the light. This is, no doubt, strengthened by the fact that, when departures are observed, they appear to be quite irregular and so may be put down to peculiarities of the individual cell rather than to anything fundamental.[4]

2-9. The Time Factor in Photoelectricity.—The fact that the photoelectric current always starts immediately when the surface is illuminated is one of the many facts in photoelectricity which receives a natural explanation in terms of the quantum theory, according to which a stream of radiation is a stream of small corpuscles of energy $h\nu$. If, on the other hand, the energy is uniformly spread out over the wave front, then, with very weak light, one might well expect a considerable time to elapse before the electron accumulates sufficient energy from the waves passing over it to give it the energy which experiment shows it to possess.

Thus consider blue light, whose intensity is of the order of 10^{-7} erg/sec cm^2, falling on a metal surface and giving rise to electrons of energy hc/λ where $\lambda = 4000$A. This is 5×10^{-12} erg. Assuming that the electron can absorb only the energy from an area of the wave front intercepted by the molecule to which it is attached, we see that the time necessary for it to accumulate this energy is $5 \times 10^{-12} \div (10^{-7} \times 10^{-16}) = 5 \times 10^{11}$ sec, which is over 15,000 years! Rayleigh[5] pointed out that, on the electromagnetic theory, a simple infinitely small resonator absorbs energy from an area of the wave front of the order of λ^2. In our case this would be $(4000 \times 10^{-8})^2$ sq cm, which is approximately 10^{-9} sq cm. On this basis, the time required would be 10^4

[1] J. Kunz and J. Stebbins, *Phys. Rev.*, **7**, 62 (1916).

[2] J. Kunz, *Astrophys. Jour.*, **45**, 69 (1917); *Phys. Rev.*, **9**, 175 (1917).

[3] N. R. Campbell and E. G. New, *Jour. Sci. Instr.*, **3**, 2 (1925).

[4] Since this section was written, the following papers related to it have appeared: "The Relation between the Photoelectric Current and the Light Intensity" by G. Kortüm (*Phys. Zeits.*, **32**, 417 [1931]) and "The Applicability of Photoelectric Cells to Photometry" by H. E. Ives and E. F. Kingsbury (*Jour. Opt. Soc. Amer.*, **21**, 541 [1931]).

[5] Lord Rayleigh, *Phil. Mag.*, **32**, 188 (1916).

sec, or several hours. Yet, with light of less energy than this, Elster and Geitel found a photoelectric effect to appear simultaneously with the illumination. No evidence has been obtained showing that there is a measurable lag in the photoelectric current from a surface after the illumination has begun, nor does the photoelectric current continue after the light has been cut off.

Marx and Lichtenecker[1] investigated the effect of illuminating a photoelectric cell intermittently. A very sensitive photoelectric cell was illuminated by the light reflected from a revolving mirror whose rate of revolution could be varied. By increasing the speed of rotation, the amount of radiation, I, falling on the surface per flash would be diminished; but the number of flashes per second, N, would be increased in such a way that the total energy received per second would be the product IN, which is a constant. By increasing the speed of rotation, the time of illumination could be cut down to 10^{-7} sec, during which interval the surface was receiving energy at the rate of 0.56 erg/sec cm^2. The photoelectric current was independent of the speed of rotation, showing that the intermittency had no effect so long as the integrated energy received by the surface was kept constant. (A photoelectric cell differs in this respect from a photographic plate, in which the blackening is a function of the intermittency as well as of the total energy falling on it.) Thus there is no indication of a possible "accumulation time" as large as 10^{-7} sec, during which the surface receives energy without emitting photoelectrons.

Lawrence and Beams[2] have devised a beautiful method for studying the effect of illuminating a photoelectric cell for very short intervals. Two crossed Nicols are interposed between a spark gap and a photoelectric cell. In between the Nicols are two Kerr cells which are essentially two flat electrodes in carbon disulphide. Double refraction is set up in the liquid when an electric field is produced between the electrodes which disappears when the field is removed. The two Kerr cells are actuated in such a way that they form, in combination with the crossed Nicols, a kind of optical shutter which opens for a period of 10^{-8} sec and then closes. The photoelectric cell is connected so that the permanently applied potential difference prevents the escape of photoelectrons. A large transient potential difference, however, is set up by the spark so as to permit the escape of photoelectrons during a short interval of time. By methods developed in the technique of electric waves, it was possible to control the time intervals between the timing of the optical shutter, the timing of the transient potential difference in the cell, and that of the spark. They conclude that the photoelectric current begins in less time than 3×10^{-9} sec after the beginning of the illumination of the surface. Also the photoelectric current ceases instantaneously after the cutting off of the illumination to within the errors of experiment (10^{-8} sec). They point out that experiments on the nature of excitation of gas atoms indicate that such atoms remain in the excited state for a small but finite time before reemitting the radiation. Since ionization, and therefore the photoelectric effect, may be regarded as an extreme form of excitation in which, however, the energy

[1] E. Marx and K. Lichtenecker, *Ann. d. Phys.*, **41**, 124 (1913).

[2] E. O. Lawrence and J. W. Beams, *Phys. Rev.*, **32**, 478 (1928).

is given out in the form of an electron instead of a quantum, they suggest that the photoelectric current might conceivably persist a short but appreciable time after the illumination is stopped. The interval, if any, is less than 10^{-8} sec. (Possibly the act of ionization corresponds more closely in excitation to the transfer of an electron to a virtual orbit. The time interval measured in the excitation experiments almost always refers to the stay in the virtual orbit and not to the time taken to move into that orbit, which is generally taken to be immeasurably small.)

2-10. Fluctuations in Photoelectric Currents.—In most photoelectric experiments the electrons emitted are numerous enough to behave like a continuous stream of electricity whose magnitude alters with the intensity of the illumination without appreciable lag. In particular, when the illumination is held constant, the flow of photoelectrons also appears to be perfectly constant. If, however, the photoelectrons were emitted at random, we should expect to find the number emitted in any given time interval to fluctuate about a mean value. The fluctuations would be relatively greater, the smaller the time interval or the smaller the mean current. The *shot effect* in thermionic emission is a well-known analogous effect. (The fluctuations are a direct consequence of the fact that the emitted electrons have a finite charge: their magnitudes may be used to determine e.)

If the electrons are emitted at random, the mean fluctuations in the photoelectric emission may be obtained from the theory of statistics. Let

n_0 = average number of electrons emitted in the interval t.

n = actual number emitted in any one interval t.

$|n - n_0|$ = absolute deviation from the average.

$\overline{|n - n_0|}$ = mean absolute deviation from the average.

$\dfrac{\overline{|n - n_0|}}{n_0}$ = mean relative deviation, or fluctuation; when multiplied by 100, it is the percentage fluctuation.

Statistical theory states that the mean relative fluctuation

$$\bar{\epsilon} \equiv \frac{\overline{|n - n_0|}}{n_0} = \frac{1}{\sqrt{n_0}}.$$

How does this affect "ordinary" photoelectric currents? Consider a current of 1.6×10^{-15} amp, *i.e.*, 10^4 electrons/sec. The mean relative fluctuation in the emission in successive seconds would be $\bar{\epsilon} = 1.0$ per cent, no matter how constant the illumination. Such a fluctuation is seldom noticed, partly because the time constants of the current-measuring device are such that it is rarely quick enough to follow the changes in current, second by second. For electrometers which are just capable of following changes in successive intervals of 10 sec each, $\bar{\epsilon} = 0.3$ per cent for the same current.

Fluctuations in photoelectric emission were first observed by Elster and Geitel.[1] They used a potassium cell, filled with argon, connected to a

[1] J. Elster and H. Geitel, *Phys. Zeits.*, 17, 268 (1916).

quick-acting fiber electrometer as shown in Fig. 2-17. On increasing the voltage across the cell to a value just under that at which the discharge passed in the dark, they observed that the electrometer fiber moved by small jumps, at irregular time intervals. These jumps were due to the emission of individual electrons (due perhaps to slight radioactivity within the cell or to γ-rays from outside), the effect of each electron being magnified through ionization by collision. On allowing a trace of light to fall on the cell, the frequency of the jumps was much increased. It was shown that the increase in the frequency of the jumps was proportional to the intensity of the light—thus establishing the proportionality rule in the region where actually the individual electrons could be counted. A measurable increase in the frequency of the jumps was produced by blue light whose intensity was as low as 3.0×10^{-9} erg/sec cm^2.

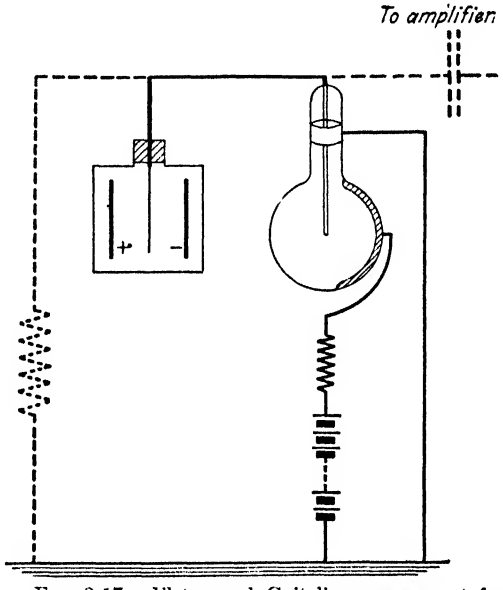

FIG. 2-17.—Elster and Geitel's arrangement for detecting emission of individual photoelectrons. (Rajewsky's arrangement indicated by the addition of the broken line.)

Elster and Geitel noticed that a photoelectric cell of the type used in the experiments just described, with a silver cathode but without any alkali metal, was insensitive to daylight *before* the passage of a discharge but became sensitive *after* a discharge had been passed through it. Such cells could be used in place of the potassium cells in the foregoing investigations. They attributed the sensitivity to the decomposition of traces of compounds of alkali metals resulting in a thin film of free alkali metal. The same effect was also obtained in cells in which a trace of NaCl had been deposited on the silver. These appear to be the first results on record relating to the high sensitivity of cells containing thin films of alkali metals (see Sec. **5-3**, **5-11**, and **12-2**).

Steinke[1] has made a careful quantitative study of the fluctuations of photoelectric currents. He used a gas-filled potassium cell in conjunction with a very sensitive Hoffmann electrometer (2000 electrons/mm). He measured the mean relative fluctuation in the electron emission in successive time intervals, $\bar{\epsilon}$ (exp), when the cell was illuminated by a steady source. Then, knowing the number of photoelectrons emitted, it was possible to calculate the theoretical value, $\bar{\epsilon}$ (calc), because this is equal to

[1] E. STEINKE, *Zeits. f. Phys.*, **38**, 378 (1926).

$1/\sqrt{n_0}$, where n_0 is the average number of photoelectrons measured in the interval under consideration. So long as the amplification factor, resulting from ionization by collision in the gas, did not exceed 60, $\bar{\epsilon}$ (exp)/$\bar{\epsilon}$ (calc) was approximately equal to 1.

It is reasonable to infer that the amplification factor was a constant, *i.e.*, ionization by collision does not superimpose any additional fluctuations. When, however, the amplification factor was raised to 600, by increasing the voltage across the cell, $\bar{\epsilon}$ (exp)/$\bar{\epsilon}$ (calc) rose to about 8, showing that when the ionization by collision is very large, it then contributes large fluctuations.

The agreement of $\bar{\epsilon}$ (exp) with $\bar{\epsilon}$ (calc) incidentally proves that the assumed value of the charge on the electron is correct to within the errors of experiment. It is to be noted that the fluctuations refer to the random *emission of electrons* and not to the random *absorption of quanta*. Since we know that the "yield" is usually less than one electron per 1000 quanta, the mean relative fluctuation would have been about $\sqrt{1000}$ less, had we been concerned with the bombardment of the surface by quanta distributed in time at random and had the emission of photoelectrons been strictly proportional to the number of quanta absorbed in the microscopic as well as in the macroscopic sense.

Rajewsky[1] has recently carried out an investigation similar in principle to that of Elster and Geitel. Instead of the usual photoelectric cell he used a Geiger-Müller tube, lined with a metal sensitive to the ultraviolet. His arrangement was similar to that of Elster and Geitel (Fig. 2-17), except for the fact that he shunted the electrometer to ground by a very high resistance. The electron emissions would then record as jumps of the electrometer fiber, which, because of the high-resistance shunt, returned to zero between each jump. The Geiger-Müller tube was also connected to an amplifier with a loud-speaker at the output end, allowing one to "hear" the emission of each electron. The character of the fluctuations is shown in Table 2-2, in which the presentation of the results differs from that of Rajewsky himself. The third column is called the "Absolute Deviation" and not the average absolute deviation, because there is no explicit statement to the effect that many observations were made from which an *average* could be computed. Nevertheless, $\bar{\epsilon}$ (exp) and $\bar{\epsilon}$ (calc) are of the same order, thus confirming the result found by Steinke. As a detector of feeble illumination, Rajewsky's apparatus is the most sensitive on record (Sec. **12-14**).[2]

The same phenomenon has been observed qualitatively by Derieux and by Kelly.[3] They introduced a minute droplet of mercury, shellac,

[1] B. Rajewsky, *Phys. Zeits.*, **32**, 121 (1931).

[2] Work along parallel lines has recently been reported by Kingsbury (*Phys. Rev.*, **38**, 1458 [1931]) in a paper entitled "Shot Effect in Photoelectric Currents."

[3] J. B. Derieux, *Phys. Rev.*, **11**, 276 (1928); M. J. Kelly, *Phys. Rev.*, **16**, 260 (1920).

TABLE 2-2.—FLUCTUATIONS IN PHOTOELECTRIC EMISSION
(Average rate of emission = 42.4 electrons/min)

Observation interval, minutes	Average number per interval, n_0	Absolute deviation, $\lvert n - n_0 \rvert$	Experimental per cent deviation, $\epsilon(\text{exp}) \times 100$	Calculated per cent deviation, $\bar{\epsilon}(\text{calc}) \times 100$	$\frac{\bar{\epsilon}(\text{exp})}{\bar{\epsilon}(\text{calc})}$
2	84.8	15.2	17.9	10.9	1.64
6	254.4	15.6	6.1	6.3	0.97
10	424	18.0	4.2	4.8	0.87
20	848	16.0	1.9	3.4	0.57

or sulphur between the plates of the condenser in an apparatus identical with that used by Millikan in his determination of e. As these droplets were usually charged to begin with, it was possible by means of a suitable electric field to hold one at rest against the pull of gravity so long as the charge remained constant. The escape of a single photoelectron from a droplet, suitably illuminated, was revealed at once by a breakdown of the equilibrium. Various time lags between the beginning of the illumination and the instant at which the photoelectron is ejected, amounting sometimes to 50 sec, were observed. The droplet is so small, and its threshold is so far in the ultra-violet, that it intercepts but few high-energy quanta per second. Then also, on the average, probably over 1000 quanta must be absorbed before one photoelectron happens to escape. Hence it is that the interval between the emissions of photoelectrons may be of the order of a minute.

CHAPTER III

THE PHOTOELECTRIC THRESHOLD

One of the chief problems which has engaged the attention of investigators ever since the discovery of the photoelectric effect is the study and comparison of the photoelectric properties of different substances, particularly the metallic elements and their alloys. For this purpose the early investigators simply measured the "saturated" photoelectric current excited in different surfaces by a source of light of constant energy. Since no two observers used sources which were exactly the same, and since the conditions under which measurements were made differed widely, it is not surprising that many conflicting results were obtained. It becomes necessary then to consider just how the photoelectric properties of a given surface may be most accurately and conveniently specified.

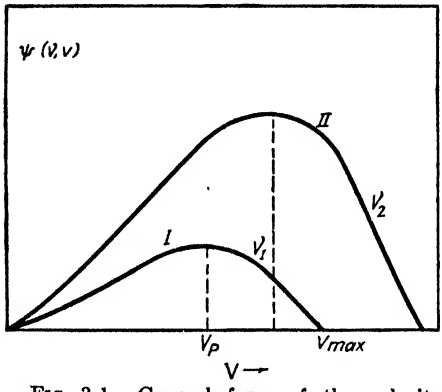

FIG. 3-1.—General form of the velocity distribution function for two values of the incident frequency, $\nu_2 > \nu_1$.

3-1. The Velocity Distribution Function.—Strictly speaking, the photoelectric properties of a surface would be completely specified only if we knew the number of electrons of any velocity v, which would be ejected from the surface by unit intensity of absorbed light of any frequency ν. If dn is the number of electrons with velocities between v and $v + dv$ ejected per unit time by unit intensity of light,[1] whose frequency is between ν and $\nu + d\nu$, then, in general,

$$dn_v = \Psi(\nu, v)d\nu dv \tag{3-1}$$

The function Ψ is called the velocity distribution function. Experiment[2] shows that this function depends upon (1) the magnitude and direction of the velocity v, (2) the frequency ν, (3) the state of polarization and angle of incidence of the light, and (4) the nature of the surface. The type of dependence on v is illustrated by curve I of Fig. 3-1, which is

[1] Leaving aside for the present any effects due to the plane of polarization and angle of incidence of the light. We must regard v, however, as a vector whose magnitude and direction must both be specified.

[2] See Chap. IV for a more complete discussion of the experiments.

drawn for a particular frequency, ν_1. If light of a greater frequency, ν_2, is used, the curve is shifted to the position II. It will be seen that in either case electrons are ejected with all velocities from zero up to a maximum v_m where v_m as we have seen in the previous chapter is calculated from the Einstein equation

$$\tfrac{1}{2}mv_m^2 = h\nu - p = h\nu - h\nu_0. \tag{3-2}$$

There is a definitely marked most probable velocity v_p, which is also a linear function[1] of ν.

The dependence of $\Psi(\nu, v)$ on the nature of the surface is very complicated, but Eq. (3-2) shows that it will certainly depend on the value of ν_0, the threshold frequency of the surface. The effects of the polarization and incident angle of the light will be discussed in Chapter V.

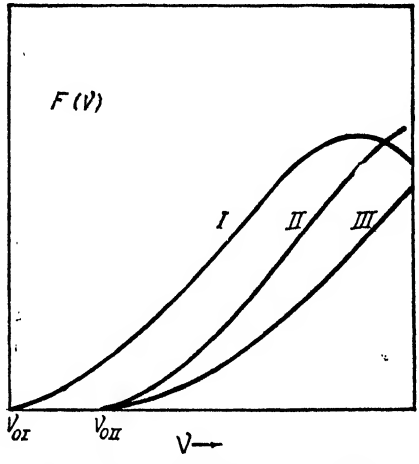

FIG. 3-2.—General form of the spectral distribution function for three different surfaces.

3-2. The Spectral Distribution Function.—If Eq. (3-1) is integrated with respect to v from 0 to v_m, we obtain

$$dn_\nu = F(\nu)d\nu$$

where dn_ν is now the total number of electrons of all velocities ejected in unit time by unit intensity of absorbed light of the frequency range between ν and $\nu + d\nu$. $F(\nu)$ is a new function which now depends only on the frequency and polarization of the light and on the nature of the surface, and is usually called the *spectral distribution function.* Its dependence on ν is shown in Fig. 3-2. For frequencies less than ν_0 there is no emission of electrons, while for greater frequencies the emission increases steadily, in some cases going through a maximum. Different metals in general show different values of ν_0 (curves I and II), though two metals may have nearly the same value of ν_0 and yet yield spectral distribution curves which do not coincide (*e.g.*, II and III).[2] The ordinate of the spectral distribution curve at any frequency represents the rate at which electrons are ejected by unit intensity of absorbed light of that frequency. This quantity is referred to as the *spectral sensitivity* or as the *photoelectric yield.* It is expressed most commonly in coulombs per calorie or in amperes per watt. When reduced to "number of electrons per absorbed quantum" it is called the *quantum efficiency* or *quantum yield.*

[1] F. WOLF, *Ann. d. Phys.*, **83**, 1001 (1927). See Sec. 4-6.

[2] See Chap. IV for a more detailed discussion.

The dependence of the spectral distribution curves on the nature of the surface is also indicated in Fig. 3-2. In going from one metal to another, the curves may be shifted parallel to themselves and also changed in slope. The amount of parallel shift depends simply on the difference in threshold frequencies of the two surfaces. Little is known in regard to the factors which affect the slope of the curves, though it is obvious that they have to do with the number of electrons in the surface which are capable of absorbing the incident quanta.

3-3. The Significance of ν_0.—It is evident from the above simple analysis that in describing and comparing the photoelectric properties of surfaces, the most important parameter[1] referring to the nature of the surface itself is its threshold frequency. Various surfaces can be most conveniently compared in terms of this quantity, so that it is an experimental problem of great importance to measure ν_0 for as many different materials as possible. We shall discuss in this chapter some of the results of such measurements, and some of the factors which cause variations in ν_0 for a given surface.

We have already seen that ν_0 is the smallest frequency of light capable of causing the ejection of electrons from the surface. In most cases it is more convenient to specify the corresponding wave-length λ_0, which is referred to as the threshold wave-length, the long wave limit, or simply as the red limit.

From the Einstein equation, $h\nu_0$ is also the least energy lost by an electron as it leaves the surface of the metal. This may be written as ϕe, where e is the electronic charge and ϕ is the effective potential jump through which the electron passes as it leaves the surface. ϕ is called the *photoelectric work function* of the surface and is of prime importance not only in the study of photoelectric phenomena but also in any study of the nature of surface forces. The relation between ϕ, ν_0, and λ_0 is,

$$\phi e = h\nu_0 = \frac{hc}{\lambda_0}.$$

If ϕ is in volts and λ_0 in Angström units, we have,[2]

$$\phi = \frac{12{,}336}{\lambda_0}.$$

In view of the fundamental importance of the photoelectric threshold in specifying the photoelectric properties of various materials, it is rather

[1] On the Sommerfeld electron theory there are two parameters depending on the nature of the surface, W_a and μ, which are discussed in Chap. VI. Since, however, μ can be *computed* if the number of free electrons per unit volume is known and since $h\nu_0 = W_a - \mu$, it is evident that ν_0 is still the most important *experimental* quantity referring to the nature of the surface.

[2] The value 12,336 ± 5 volt-A is the most probable value of this constant hc/e as given by R. T. Birge, *Phys. Rev., Suppl.* **1**, 1 (1929). For obvious mnemonic reasons, however, the value 12,345 is often used and is sufficiently close to the most probable value for most purposes.

disappointing to find that the measured values of this quantity for a given material vary over wide limits, depending on the conditions under which the measurements are made. This is due to the fact that the work done by an electron in leaving a surface is determined by the nature of the outermost surface layers, and hence will be very greatly influenced by the structure of the surface and by the presence of traces of surface impurities. In particular, the presence of small amounts of occluded gases in a metal surface may exert a profound influence on the threshold. Since the removal of gas layers can be accomplished, if at all, only by the most drastic treatment, the problem of determining the photoelectric thresholds of the pure metals is one of extraordinary difficulty. As a result we find that, in spite of the vast amount of experimental work which has been done on this problem, there are only a very few metals for which the work function characteristic of the metal itself is known with any accuracy. During the past few years, however, rapid improvements in experimental technique have been made, and more rapid progress in this field may now be expected.

EXPERIMENTAL METHODS OF DETERMINING THE PHOTOELECTRIC THRESHOLD

3-4. The Stopping-potential Method.—The determination of the photoelectric threshold by making use of the Einstein equation has already been discussed in the previous chapter in connection with the experimental tests of this equation. The procedure in measuring ν_0 is to measure the maximum emission energies, or stopping potentials, of the electrons ejected from the given surface by monochromatic light of several different frequencies. Plotting the stopping potentials (corrected for contact potential) as a function of ν, a straight line is obtained whose intercept on the frequency axis is ν_0 (see Fig. 2-12, page 21).

As we have seen, elaborate precautions are necessary to eliminate scattered light of shorter wave-length than that which the monochromatic illuminator is set to isolate, and also to correct for the contact potential between the illuminated surface and the receiving electrode. When proper precautions are taken, however, this method for determining ν_0 can be made to yield results of considerable precision, as is illustrated by the work of Millikan[1] and his associates and of Lukirsky and Prilezaev.[2] In general, however, measurements of stopping potentials are difficult to make, and for this reason most of the determinations of ν_0 have been made by other methods.

3-5. Determination of ν_0 from Spectral Distribution Curves.—This is the most commonly used method and can be readily understood by referring to Fig. 3-2. If the photoelectric yield, as defined in Sec. 3-2, is measured for the given surface for a series of different frequencies, the

[1] R. A. Millikan, *Phys. Rev.*, **7**, 355 (1916).

[2] P. Lukirsky and S. Prilezaev, *Zeits. f. Phys.*, **49**, 236 (1928).

values can be plotted into a spectral distribution curve. The point at which the extrapolated curve plunges into the frequency axis gives the desired threshold ν_0. Typical experimental curves are shown in Fig. 3-3, in which, following the more common practice, the yield is plotted against incident wave-length instead of frequency. The intercept of each gives λ_0, the long wave limit.

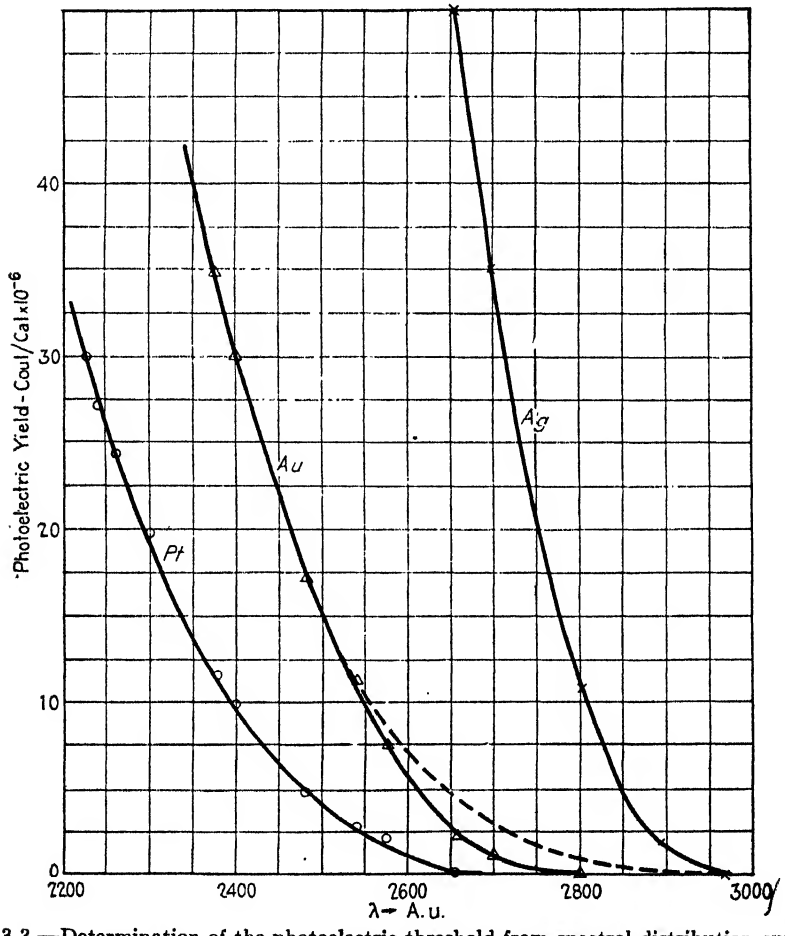

FIG. 3-3.—Determination of the photoelectric threshold from spectral distribution curves (*Suhrmann*). The broken line shows the effect of scattered light.

In making measurements of photoelectric efficiency, a surface of the metal under test is suitably mounted in vacuum so that it may be illuminated by light of frequency not too far from the threshold. Except for the alkali metals, ultra-violet light is usually required. A collecting electrode is provided which is given a positive potential with respect to the illuminated surface, sufficient to collect all the ejected electrons. The current reaching the receiving electrode is measured by means of

an electrometer or galvanometer. Various arrangements which have been used by different observers are shown in Figs. 3-9, 3-11, and 3-15.[1]

It is also necessary in this method that the incident light be truly monochromatic, in particular that no scattered light of short wave-length be present. For this purpose the monochromatic illuminator must be supplemented by filters opaque to short wave-lengths. Some observers have found it desirable to use two illuminators in series. The presence of scattered light of short wave-length causes the spectral distribution curve to show a pronounced "foot" as indicated by the dotted line in Fig. 3-3, giving an apparent threshold farther toward the longer wave-lengths than the true value. The relative intensity of the various spectral lines furnished by the light source must be known and can be measured by means of a sensitive thermopile. In order to reduce the measurements to unit intensity of *absorbed* light, it is necessary to know also the reflectivity of the surface. In many cases it is assumed that this does not change appreciably with wave-length over a limited range, in which case its value need not be known, since it will have no effect on the threshold.

3-6. The "Complete" Photoelectric Emission.—A less direct but very interesting and useful method for measuring the photoelectric threshold has recently been developed independently and along somewhat different lines by Roy[2] and Suhrmann.[3] These authors make use of a relation developed in 1912 by Richardson,[4] which has received further theoretical and experimental treatment at the hands of W. Wilson,[5] in 1917, and A. Becker,[6] in 1919.

Richardson showed from thermodynamical reasoning that if a metal surface be exposed to the total thermal radiation from a black body at a temperature T, the total photoelectric current from the surface should vary with T according to the equation,

$$I = A_1 T^2 \epsilon^{-\frac{h\nu_0}{kT}} = A_1 T^2 \epsilon^{-\frac{b}{T}} \tag{3-3}$$

where ν_0 is the threshold frequency of the illuminated surface, A_1 is a constant, and b is an abbreviation for the quantity $h\nu_0/k$, k being the Boltzmann constant. It will be seen that this is identical with the Richardson equation for the thermionic emission at the temperature T from a surface whose work function is $h\nu_0/e$. There is thus a close relation, to be discussed more fully in Chapter VI, between thermionic emission and the photoelectric emission induced by black-body radiation. The photo-

[1] The technique of making photoelectric measurements is discussed in detail in Chap. XII.

[2] S. C. Roy, *Proc. Roy. Soc.*, **112**, 599 (1926).

[3] R. Suhrmann, *Zeits. f. Phys.*, **33**, 63 (1925).

[4] O. W. Richardson, *Phil. Mag.*, **23**, 615 (1912); **24**, 570 (1912). The derivation is given in Sec. **6-10**.

[5] W. Wilson, *Proc. Roy. Soc.*, **93**, 359 (1917).

[6] A. Becker, *Ann. d. Phys.*, **60**, 30 (1919).

electric current obtained under these conditions has been called the "complete" photoelectric emission.

Equation (3-3) can be tested by measuring the complete photoelectric emission for various values of the temperature of the illuminating body and then plotting log I/T^2 as a function of $1/T$. If the equation is

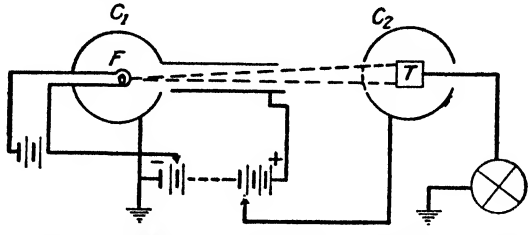

FIG. 3-4.—Apparatus for study of complete photoelectric emission. (*Roy.*)

satisfied, a straight line is obtained whose slope is equal to $-b = -h\nu_0/k$, from which ν_0 is at once determined. Wilson, using sodium surfaces,

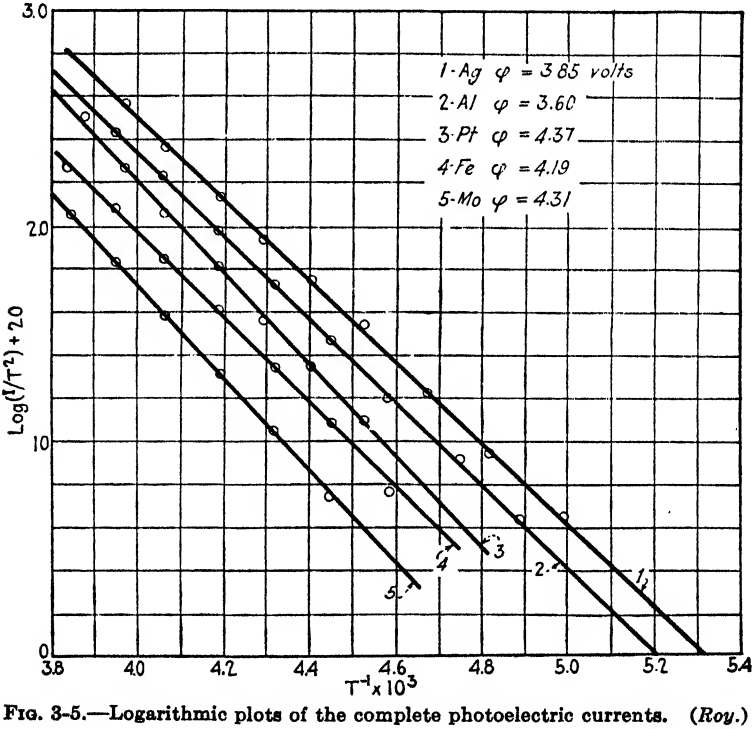

FIG. 3-5.—Logarithmic plots of the complete photoelectric currents. (*Roy.*)

made such measurements and showed that the relation between I and T was really of this form, a conclusion which was confirmed by Becker.

The apparatus used by Roy for measuring photoelectric thresholds by this method is shown in Fig. 3-4. The source of light was a tungsten filament F whose temperature can be determined from measurements of

its resistance using the data of Worthing.[1] The emissivity of tungsten being known, the departure of its radiation from true black-body radiation can be calculated. The filament is given a positive potential with respect to the cylinder C_1 which nearly surrounds it, in order to prevent the emission of electrons when it is heated. The beam of radiation passes between two parallel plates across which a potential is applied which serves to remove any stray electrons or positive ions. Photoelectrons are ejected from the cathode T and collected by the cylinder C_2. The cathode was arranged so that plates of four different metals could be mounted upon it and each brought in succession into the path of the incident light. Measurements were reported on 11 different metals, and the linear relation between $\log I/T^2$ and $1/T$ was found to hold in every case. Curves for five metals are shown in Fig. 3-5. There is good agreement between the values of ν_0 calculated from the slopes of these curves and the values obtained by other methods. The values of A_1, b, ϕ, and λ_0, obtained by Roy, are collected in Table 3-1. Since the surfaces were given no outgassing treatment, these values cannot be taken as characteristic of the pure metals.

TABLE 3-1.—VALUES OF THE CONSTANTS IN "COMPLETE" PHOTOELECTRIC EMISSION

Metal	A_1, amp/cm² deg²	b, °K	ϕ, volts	λ_0, A.u.
Al	1.06×10^{-10}	42380	3.65	3380
Zn	1.78×10^{-10}	43630	3.76	3280
Ag	1.94×10^{-10}	44620	3.85	3210
Pt	1.39×10^{-9}	51340	4.42	2790
Fe	2.86×10^{-10}	48630	4.20	2940
Mo	2.84×10^{-10}	50140	4.31	2860
C	1.78×10^{-9}	55250	4.76	2590
Ta	1.98×10^{-10}	45540	3.93	3140
W	8.99×10^{-10}	52440	4.51	2730
Ni	5.24×10^{-10}	47840	4.12	2990
Au	1.99×10^{-9}	54610	4.71	2620

3-7. Suhrmann's Method.—Suhrmann has also made use of Eq. (3-3), though he did not employ black-body radiation directly. Instead he made use of the fact that the complete photoelectric current from a surface can be computed if the spectral distribution function $F(\nu)$ is known by means of the equation

$$I = \int_0^\infty F(\nu)\, E(\nu) d\nu,$$

where $E(\nu)$ is the distribution function (of Wien[2] or Planck) for the energy radiated by a black body. Suhrmann determined experimentally the

[1] A. G. WORTHING, *Phys. Rev.*, **19**, 436 (1922).

[2] For the wave-lengths effective in photoelectric emission the Planck law does not differ appreciably from that of Wien.

form of the function $F(\nu)$ and, using Wien's distribution law, performed the above integration graphically. In Fig. 3-6, curve I is the observed photoelectric spectral distribution curve for a silver surface. The other curves were obtained by multiplying the ordinates of curve I at each frequency by the value of $E(\nu)$ for that frequency and for a particular temperature T. The area under each curve is the complete photoelectric emission which would be excited by a black body at the temperature T. The "complete" photoelectric current I is thus obtained for a series of temperatures. Plotting $\log I/T^2$ against $1/T$ yields a straight line, from the slope of which ν_0 is determined. A set of straight lines so obtained for silver in various stages of outgassing is reproduced in Fig. 3-7. Suhrmann's results are of interest not only in that they give a new method for determining ν_0, but also because they afford experimental proof of a relation used by Richardson[1] that the mathematical form of the function $F(\nu)$ must be such as to satisfy the equation

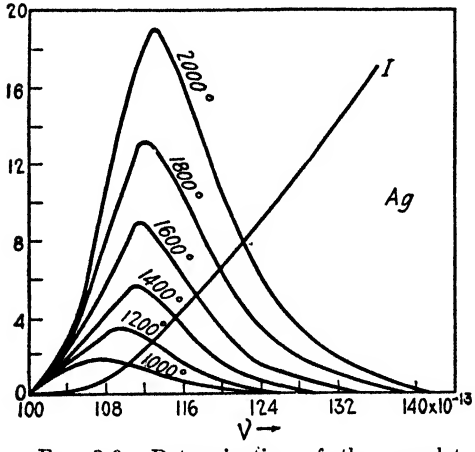

FIG. 3-6.—Determination of the complete photoelectric emission from spectral distribution curves. Curve I is the experimental curve and the others are obtained from this by multiplying the ordinates by the black-body distribution function $E(\nu)$. A different scale factor has been used for each curve.

$$\int_0^\infty F(\nu)\, E(\nu) d\nu = AT^2 \epsilon^{-\frac{h\nu_0}{kT}}$$

In a later paper Suhrmann[2] showed that his data were best satisfied by an equation in which T^n is substituted for T^2. The exponent n was found to vary somewhat, but usually had a value in the neighborhood of 4.

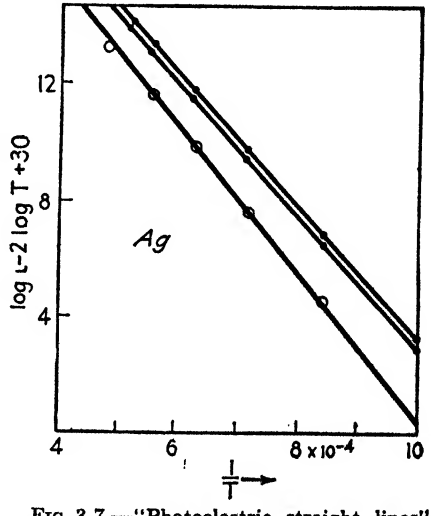

FIG. 3-7.—"Photoelectric straight lines" for silver at three stages of outgassing. (*Suhrmann.*)

3-8. Determination of ν_0 from Thermionic Data.—The energy required to remove an electron from a metal surface may also be deter-

[1] See Sec. 6-10.

[2] R. SUHRMANN, *Zeits. f. Phys.*, **54**, 99 (1928).

mined from thermionic measurements making use of the Richardson equation

$$I = AT^2\epsilon^{-\frac{b_0}{T}}$$

where T is now the temperature of the emitting body, I the saturated electron current per unit area of the surface, b_0 is equal to $\phi_t e/k$ (ϕ_t is the thermionic work function), and A is a constant. It has long been evident from the theory of photoelectric and thermionic effects that the measured values of the photoelectric and thermionic work functions should be nearly equal, though it is only recently that this conclusion has been checked experimentally with any precision.[1] It has been shown that the previous failure to obtain such agreement is due to the difficulty in obtaining uncontaminated surfaces of the metals. For surfaces containing traces of gas or other impurities the two work functions may differ widely—due possibly to the fact that the work function for such a surface probably changes rapidly with temperature between room temperature, where photoelectric measurements are usually taken, and the incandescent temperatures necessary to obtain thermionic measurements. For thoroughly cleaned surfaces, however, a definite agreement between the two work functions is found, so that for such surfaces the photoelectric threshold may be calculated if the thermionic work function is known,[2] using the relation

$$\phi e = h\nu_0 = \phi_t e = b_0 k.$$

For ϕ in volts and b_0 in degrees K, we have

$$\phi = b_0 \times 8.61 \times 10^{-5}.$$

3-9. The Total Photoelectric Sensitivity.—In much of the earlier work in this field no attempt was made to determine the photoelectric thresholds and work functions of various surfaces, since their importance and significance were not fully appreciated. Surfaces were compared rather in terms of their total photoelectric "sensitivity," by which was usually meant the photocurrent excited by the total radiation from the particular source in use. The conflicting results obtained testify to the fact that this quantity is not sufficiently definite to be used as a basis of comparison of the results of different observers on different metals.

On the other hand, many observers who have been interested only in the *changes* which take place in the photoelectric properties of a given surface when it is put through a particular type of treatment have found the total sensitivity of the surface, because of its ease of measurement, a

[1] See A. H. Warner, *Proc. Nat. Acad. Sci.*, **13**, 56 (1927); L. A. DuBridge, *Phys. Rev.*, **31**, 236 (1928); M. J. Martin, *Phys. Rev.*, **33**, 991 (1929); E. H. Dixon, *Phys. Rev.*, **37**, 60 (1931).

[2] An exhaustive review of the theory and technique of thermionic measurements has recently been given by S. Dushman, *Rev. Mod. Phys.*, **2**, 381 (1930).

useful quantity to study. Much of our knowledge of the effects of gases on surfaces has been obtained through studies of this type. Moreover, it has been found that, for a given surface, if the intensity of the light source and the optical constants of the surface remain fixed, an increase in the sensitivity may often be taken as qualitative evidence of a shift in the threshold to longer wave-lengths, and *vice versa*. This is at once evident if curve I of Fig. 3-2 is imagined shifted parallel to itself toward longer wave-lengths. The photoelectric yield for all wave-lengths shorter than the threshold is increased and, in addition, a greater portion of the spectrum of the incident light becomes effective in liberating electrons. The total sensitivity is thus increased. Such an interpretation of the sensitivity changes is not always allowable, however, since a number of cases have been reported[1] in which there was observed a change of sensitivity without change of threshold. Goetz[2] has recently found that during one of the crystal changes in tin the threshold shifts to the violet, although the sensitivity to certain spectrum lines increases rather than decreases. Such cases are possibly rare, but they emphasize the desirability of obtaining measurements on the *threshold* directly whenever possible.

Estimates of the photoelectric threshold have been obtained by measuring the sensitivity of the surface to limited portions of the spectrum by introducing filters in the path of the incident light.[3] If a series of filters is available whose short wave-length transmission limits are fairly sharp, they may be introduced in succession into the light path, and in this way the longest wave-length which will produce a measurable photoelectric emission is determined. This method, in spite of its lack of precision, has the advantage of great convenience, particularly where changes in the surface are being studied.

THE PHOTOELECTRIC THRESHOLDS OF THE METALS AND THE EFFECTS OF GASES

It has already been mentioned that the electron work function of a surface is determined chiefly by the outermost layer of atoms, so that superficial surface conditions play a predominating rôle in the study of photoelectric thresholds. In fact, it is usually true that the threshold observed under ordinary conditions is characteristic not of the nature of the metal but merely of the instantaneous condition and previous history of the surface. The long wave limit may be shifted over wide limits by even slight changes in the gas content of the surface. It is

[1] W. B. Hales, *Phys. Rev.*, **32**, 841 (1928); A. H. Warner, *Phys. Rev.*, **33**, 815 (1929); E. H. Dixon, *Phys. Rev.*, **37**, 60 (1931).

[2] A. Goetz, *Phys. Rev.*, **33**, 373 (1929).

[3] R. C. Williamson, *Phys. Rev.*, **21**, 107 (1923); L. A. DuBridge, *Phys. Rev.*, **29**, 451 (1927); T. M. Dahm, *Jour. Opt. Soc. Amer.*, **15**, 261 (1927); E. H. Dixon, *Phys. Rev.*, **37**, 60 (1931).

therefore a problem of great importance to determine the factors which cause the work function to vary and to learn how spurious variations may be eliminated and the true values characteristic of the metal itself be obtained.

3-10. Photoelectric "Fatigue."—One of the first observations made by Hallwachs[1] in his pioneer work on the photoelectric effect was that the photocurrent from a freshly scraped zinc plate in air spontaneously decreased in the course of time, and in some cases finally disappeared altogether. This "aging" effect was found to take place more rapidly when the surface was continuously illuminated than when kept in the dark and it was therefore given the name of "photoelectric fatigue" (*Ermüdung*). Hallwachs' conclusions were confirmed by later observers,[2] and in the years immediately following 1900 a large number of investigations were carried out to determine the nature and causes of fatigue, most of the experiments being carried out in air and other gases at atmospheric pressure. Hallwachs[3] himself, however, was the first to show that the aging of a surface was in reality not a true fatigue effect, but was due principally to the occlusion of gases by the active surface. The effect of light in increasing the rate of fatigue was shown to be due to photochemical processes such as the production of ozone or possibly of H_2O_2, which greatly affected the emission from the surface. These conclusions were amply verified by later experiments.[4]

In their attempts to eliminate the disturbing effects of gases, the earliest experimenters, led by Lenard[5] in 1902, carried out their photoelectric experiments in vacuum. However, it at once appeared from the conflicting results obtained that the troublesome effects could not be so easily eliminated; for the effects in vacuum were, if anything, more complicated than those in air. Some observers[6] reported no fatigue effects, while others[7] found them very marked. During the next few years extensive studies of photoelectric fatigue in vacuum were made by many observers.[8] As a result of these, it became quite clear that the changes in the photoelectric properties of surfaces in vacuum were not a true fatigue but were again caused by residual gases occluded in the

[1] W. Hallwachs, *Wied. Ann.*, **33**, 308 (1888).

[2] H. Kreusler, *Ann. d. Phys.*, **6**, 398 (1901); H. Buisson, *Ann. Chim. et Phys.*, **24**, 320 (1901).

[3] W. Hallwachs, *Phys. Zeits.* **5**, 489 (1904).

[4] E. Ullmann, *Ann. d. Phys.*, **32**, 15 (1910); H. S. Allen, *Proc. Roy. Soc.*, **82**, 164 (1909), *Phil. Mag.*, **20**, 565 (1910).

[5] P. Lenard, *Ann. d. Phys.*, **8**, 149 (1902).

[6] J. Elster and H. Geitel, *Wied. Ann.*, **48**, 627 (1893); E. v. Schweidler, *Phys. Zeits.*, **4**, 136 (1902); R. A. Millikan and G. Winchester, *Phil. Mag.*, **14**, 188 (1907).

[7] E. Ladenburg, *Ann. d. Phys.*, **12**, 558 (1903); J. Robinson, *Phil. Mag.*, **23**, 255 (1912).

[8] A more detailed history of the problem of photoelectric fatigue will be found in H. S. Allen, "Photoelectricity," Chap. XII.

surface itself or in the walls of the containing vessel. In many cases the effects were enhanced by the photochemical action of the incident light,[1] but for the most part they were spontaneous changes unaffected by light. It has now been thoroughly established that a pure metal surface in an extremely high vacuum shows no change in its photoelectric sensitivity, and hence photoelectric fatigue in the true sense of the word does not exist. The term fatigue is still used by many writers, however, as a convenient name to apply to *any* spontaneous change in the photoelectric properties of a surface, whether it be due to the presence of gas, to photochemical effects, or to any other effects which may or may not be caused by the incident light.

Studies of the effects of gases and other surface impurities on photoelectric emission occupy a prominent place in the photoelectric literature of the past 30 years. It will be necessary to review briefly the results of these studies.

3-11. Is the Presence of Gas Necessary for the Photoelectric Process? By 1914 it had been found by a number of observers, Fredenhagen,[2] Wiedmann and Hallwachs,[3] and Küstner[4] among others, that the removal of gas layers from certain metal surfaces (K and Zn) by cutting fresh surfaces in vacuum or by repeated distillation of the metal caused a marked decrease in the photoelectric sensitivity of the surface to the sources of light ordinarily used. It had also been found by Richardson,[5] H. A. Wilson,[6] and many others that degassing also caused a decrease in the *thermionic* current from platinum, while Hughes[7] found from contact potential measurements that gas-free zinc surfaces were considerably more electronegative than gas-filled surfaces of the same metal. The view was therefore advanced that all three of these closely related effects were conditioned entirely by the presence of gas and that the removal of the last traces of gas layers would cause both the photoelectric and thermionic effects of *all* metals to disappear. At that time there was considerable experimental evidence in favor of this view, and many later experiments seemed to confirm it. From the theoretical viewpoint, however, the "chemical action" theory was disproved by Richardson[8] as far as the thermionic effect was concerned; and the careful experiments of Langmuir[9] showed clearly that, for tungsten at least, large thermionic

[1] *Cf.* R. P. Winch, *Phys. Rev.*, **36**, 601 (1930).

[2] K. Fredenhagen, *Phys. Zeits.* **15**, 65 (1914).

[3] G. Wiedmann and W. Hallwachs, *Verh. d. Deutsch. Phys. Ges.*, **17**, 107 (1914).

[4] H. Küstner, *Phys. Zeits.*, **15**, 58 (1914); *Ann. d. Phys.* **46**, 893 (1915).

[5] O. W. Richardson, "Emission of Electricity from Hot Bodies," 2d ed., p. 118 (Longmans, Green and Co., 1921).

[6] H. A. Wilson, *Phil. Trans. Roy. Soc.*, **A208**, 251 (1908).

[7] A. L. Hughes, *Phil. Mag.*, **28**, 337 (1914).

[8] O. W. Richardson, *Phil. Mag.*, **26**, 345 (1913).

[9] I. Langmuir, *Jour. Amer. Chem. Soc.*, **38**, 2221 (1916).

currents could be obtained from the thoroughly outgassed surface. Later photoelectric experiments[1] also failed to confirm the earlier results of Fredenhagen and Wiedmann and Hallwachs on potassium and of Küstner on zinc, since it was shown that even after prolonged degassing in the highest attainable vacuum these metals still showed large photoelectric effects. These results, combined with many others which have been obtained in recent years, seem to show conclusively that the existence of the photoelectric effect is not conditioned by the presence of absorbed gases in metal surfaces. The presence of such gases does, however, have a very great influence on the value of the photoelectric threshold of most metals. As the gases are eliminated by heating in vacuum or by repeated distillation the threshold may show large changes,[2] but the evidence at present shows that it finally approaches a limiting value which is presumably characteristic of the metal itself. The determination of the true values of the thresholds of the pure metals constitutes one of the most important problems in the field of photoelectricity, and one which has engaged the attention of many investigators. We present in the following sections some of the results of these studies, taking up first those metals which have been thoroughly studied in the gas-free state. A complete tabulation of all the published values of the thresholds of the metals is given in Table 3-2, page 75.

3-12. The Photoelectric Properties of Platinum.—The photoelectric, thermionic, and related properties of platinum have probably been more extensively studied than those of any other metal. For experimental reasons it is one of the most convenient metals to choose for investigations of this type. Nevertheless, the great affinity for gas, particularly hydrogen, and the extreme electronegative character of its surface when clean have presented such serious difficulties that the reported values of the long wave limit for the "clean" metal differ among themselves by as much as 1200 A.u.

One of the first systematic studies of the behavior of the photoelectric properties of platinum during the process of removing the occluded gases was made by Piersol,[3] who sought to test the conclusions of Fredenhagen and Hallwachs[4] that if all gases were removed the photoelectric properties of the metals would disappear. Piersol measured simply the photoelectric "sensitivity" to the total radiation from a quartz mercury arc, and eliminated the gases from the specimen by continued heating in

[1] H. E. Ives, S. Dushman, and E. Karrer, *Astrophys. Jour.*, **43**, 9 (1916); R. Pohl and P. Pringsheim, *Verh. d. Deutsch. Phys. Ges.*, **16**, 336 (1914); C. E. Mendenhall and J. H. Dillon, private communication (1931). J. H. Dillon, *Phys. Rev.*, **38**, 408 (1931).

[2] R. Suhrmann (*Ann. d. Phys.*, **67**, 43 [1922]) was the first to study threshold changes.

[3] R. J. Piersol, *Phys. Rev.*, **8**, 238 (1916).

[4] *Loc. cit.*

vacuum at high temperatures. It was found that during the first stages of heating the sensitivity showed a marked increase, but further intense heating caused it to decrease again. He concluded, however, that there was a large residual effect even after long treatment which could be attributed to the platinum itself, independent of gases. The work was continued along similar lines by Welo,[1] who came to the same conclusions.

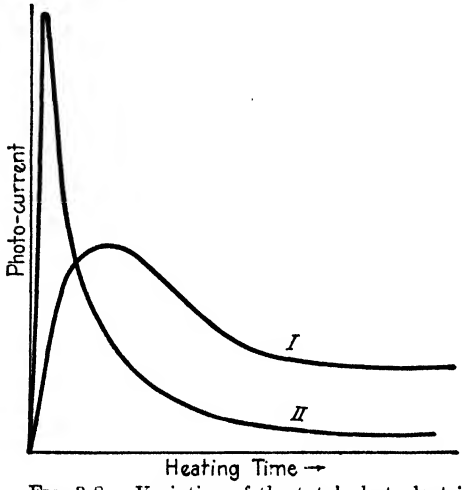

FIG. 3-8.—Variation of the total photoelectric sensitivity of Pt during outgassing by heating. I. Heating at 1000°C. II. Heating at 1600°C.

The question was examined with great thoroughness during the years 1916–1920 by Hallwachs and his students, who came to quite different conclusions. Typical curves obtained by Sende and Simon[2] are shown in Fig. 3-8. In curve I the sensitivity of the platinum specimen to the total radiation from a quartz mercury arc is plotted as a function of the time for which it was heated in vacuum at 1000°C. It will be noted that the sensitivity at first increases, passes through a maximum, and then decreases. If the temperature of heating is increased (curve II) the maximum becomes higher and sharper and the subsequent decrease more rapid. This is in agreement with the results of Piersol and Welo. It was found, however, that if the heating were continued long enough the decrease also continued, and the photocurrent approached values which in some cases were less than 0.1 per cent of the maximum value reached. Sende and Simon were thus led to the natural conclusion that if the gases could be completely eliminated from platinum no photocurrents would be observed. Hughes[3] had suggested that a more logical interpretation was simply that the threshold

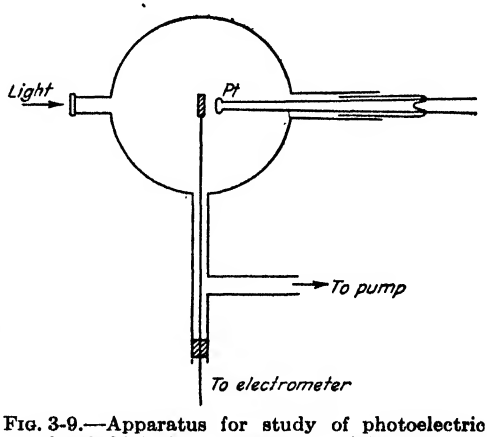

FIG. 3-9.—Apparatus for study of photoelectric threshold during outgassing. (*Suhrmann.*)

[1] L. A. WELO, *Phys. Rev.*, **12**, 251 (1918).

[2] M. SENDE and H. SIMON, *Ann. d. Phys.*, **65**, 697 (1920).

[3] A. L. HUGHES, *Nat. Research Council, Bull.* **2**, 101 (1921).

had been displaced by the outgassing to a value beyond the range of wave-lengths transmitted by quartz.

Suhrmann[1] in 1922 gave a new turn to the investigations in this field. Instead of measuring merely the photoelectric sensitivity he used monochromatic light and measured the threshold by use of the spectral distribu-

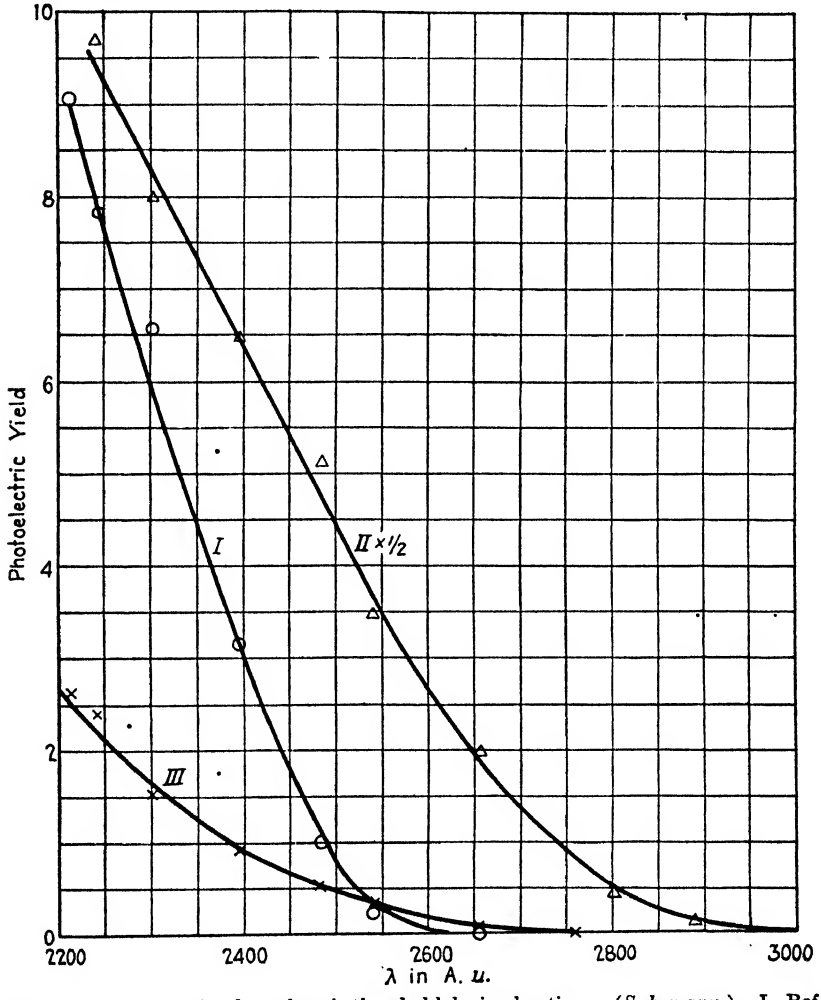

FIG. 3-10.—Change in photoelectric threshold during heating. (*Suhrmann.*) I. Before heating. II. After 10 sec at red heat (plotted to ½ scale). III. After extended heating at high temperatures.

tion curves, using the apparatus shown in Fig. 3-9. He found (Fig. 3-10) that during outgassing the long wave limit shifted first from 2600A (curve I), to 3000A (curve II), and then with further treatment back to 2700A (curve III). This constituted definite evidence that the

[1] R. SUHRMANN, *Ann. d. Phys.*, **67**, 43 (1922).

changes in *sensitivity* reported by others were to be traced directly to *threshold* shifts—the initial shift to the red corresponding to the rise in sensitivity, and the subsequent shift to the violet to the decrease in sensitivity after passing the maximum. Suhrmann took 2675A (4.61 volts) as the best value of the threshold for clean Pt.

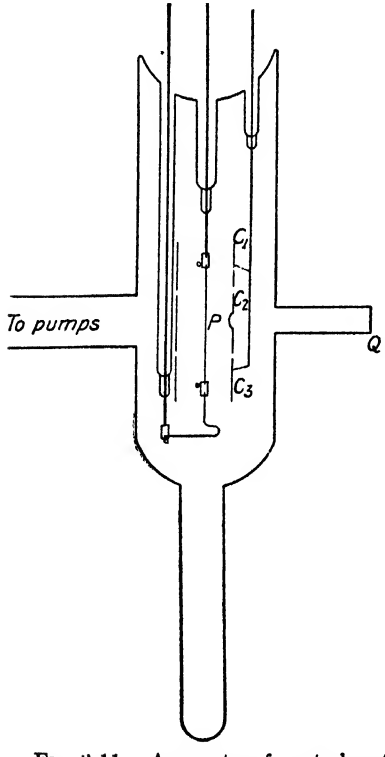

FIG. 3-11.—Apparatus for study of photoelectric and thermionic work functions of Pt. (*DuBridge.*)

A series of experiments carried out at the University of Chicago by Koppius,[1] Tucker,[2] and Woodruff[3] showed, however, that the final value of the red limit for outgassed platinum was considerably below the value 2675A given by Suhrmann. These observers employed vacuum conditions even better than those used by Suhrmann and found that, immediately after long periods of heating, the specimen was insensitive to the radiation from the quartz mercury arc. The limit of transmission of quartz is in the neighborhood of the mercury line at 1850A. In practice, however, there are but few lines in the mercury spectrum of appreciable intensity of wave-length shorter than about 2100A, so that their results can be interpreted as indicating that the threshold for clean platinum had been shifted to a wave-length shorter than this. Herrmann[4] obtained results consistent with these and with those of Sende and Simon. He found that prolonged outgassing caused the sensitivity of his platinum specimens to the mercury arc to approach extremely small values, though it did not entirely disappear.

In 1926 a series of experiments was carried out by DuBridge,[5] in which an attempt was made to determine the *final* value approached by the threshold of platinum specimens after more extended treatment in the highest attainable vacuum. For this purpose the times of heating were extended to as long as 300 hr in place of the 15 or 20 which had

[1] O. KOPPIUS, *Phys. Rev.*, **18**, 443 (1921).
[2] F. G. TUCKER, *Phys. Rev.*, **22**, 574 (1923).
[3] A. E. WOODRUFF, *Phys. Rev.*, **26**, 655 (1925).
[4] K. HERRMANN, *Ann. d. Phys.*, **77**, 503 (1925).
[5] L. A. DUBRIDGE, *Phys. Rev.*, **29**, 451 (1927); **31**, 236 (1928); **32**, 961 (1928).

previously been regarded as sufficient, while the pressures in the cell as measured by an ionization gage were reduced to as low as 10^{-8} mm Hg. A diagram of the apparatus is shown in Fig. 3-11. The tube was not essentially different from those used by previous observers[1] except

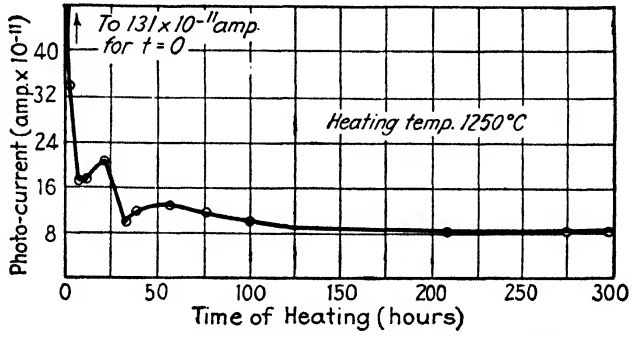

FIG. 3-12.—Changes in the total photoelectric sensitivity of Pt during extended outgassing.

that it was arranged so that all wax and grease joints were eliminated from the low-pressure side of the pumps to prevent contamination of the specimen by their vapors. The quartz window Q which served to

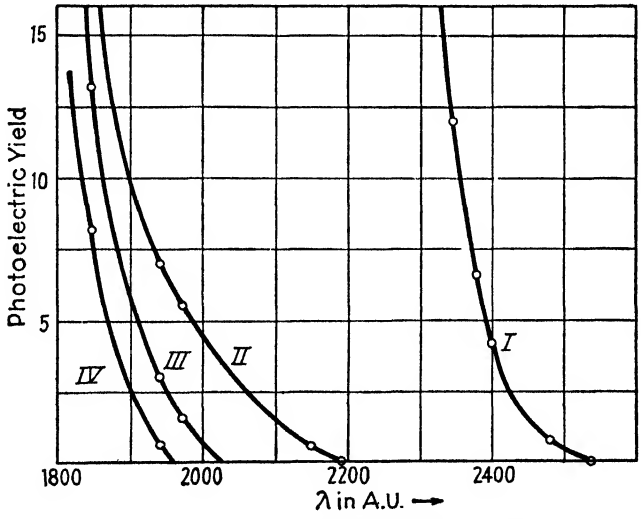

FIG. 3-13.—Spectral distribution curves for Pt during outgassing. I. Before heating. II. After 50 hr. heating. III. After 100 hr. IV. After 300 hr.

admit the ultra-violet light was sealed directly to the pyrex tube by means of a graded quartz to pyrex seal. The platinum specimen in the form of a strip of thin foil could be heated by an electric current and its temperature measured with an optical pyrometer.

The behavior, during outgassing by heat treatment, of the total photoelectric sensitivity to the radiation from a quartz mercury arc is

[1] *Cf.* R. SUHRMANN, *Zeits. f. Phys.*, **33**, 63 (1925).

shown in Fig. 3-12. It was found in all cases that the photoelectric current decreased to a limiting value, not zero, which could not be changed by further treatment. A series of spectral distribution curves obtained at various stages of the heating process is reproduced in Fig. 3-13. It will be seen that the photoelectric threshold shifted from an initial value of 2540A (curve I) to a final value of 1962A (curve IV). Many hours of additional treatment failed to cause a further shift of the curve and there was considerable evidence to indicate that the latter value was characteristic of gas-free platinum. At this stage no further evolution of gas could be detected with a sensitive ionization gage and all attempts to lower the pressure still further by immersing the tube in liquid air, by sealing off the tube from the pumps and completing the clean-up process by the electrochemical action of magnesium, or by further heat treatment at higher temperatures up to the melting point, failed to produce further changes in the threshold of any of the 15 specimens studied.

The value of 1962A for the photoelectric threshold corresponds to a work function of 6.30 volts, which is higher than the values observed for any other clean metal. It has been suggested[1] that this might be due to the presence of a film of oxide even on the supposedly clean platinum. This would of course be difficult to test directly, though the consistency of the results seems to make it quite improbable. Introduction of oxygen caused a still further increase of the work function, but it returned to the same value after a short heating in vacuum. Introducing hydrogen caused a decrease in the work function, but it again returned to the value 6.30 volts after heating in vacuum.

3-13. The Thermionic Work Function of Platinum.—Up to 1928 measurements of the thermionic work function for "clean" platinum had shown discrepancies as great as those shown in the photoelectric experiments. The values given by various observers ranged from 4.5 to 6.6 volts,[2] with the "most probable" value usually given as about 5.0 volts.[3] It was recognized, however, that the discrepancies could undoubtedly be traced to the differences in outgassing technique used by different observers, and it seemed that in general the more thoroughly cleaned surfaces exhibited the higher values of ϕ_t. Attempts to compare the thermionic and photoelectric work functions had for the most part led to inconclusive results, though Suhrmann[4] found them to have a common value of 4.57 volts for a partially degassed specimen.

Using the extended outgassing procedure previously described, DuBridge[5] made a study of the thermionic properties of platinum during

[1] L. A. Welo, *Phil. Mag.*, **2**, 463 (1926).

[2] For a complete tabulation, see S. Dushman, *Rev. Mod. Phys.*, **2**, 396 (1930).

[3] O. W. Richardson, "Emission of Electricity from Hot Bodies," p. 81.

[4] R. Suhrmann, *Zeits. f. Phys.*, **13**, 17 (1923).

[5] *Loc. cit.*

the cleaning process. It was found that the thermionic currents were even more sensitive to slight changes in the nature of the surface than the photocurrents, and it was only after sealing off the tube from the pumps and a thorough clean-up of the residual gas that consistent results were obtained. The thermionic curves for a typical specimen at various stages in the outgassing process are shown in Fig. 3-14. It will be noted that there is a steady increase in the slope and hence in the work function until a final value is reached (curve 5), which is not changed by further treatment. The best measurements gave 6.27 ± 0.05 volts as the final value for ϕ_t, and this is in remarkably good agreement with the value

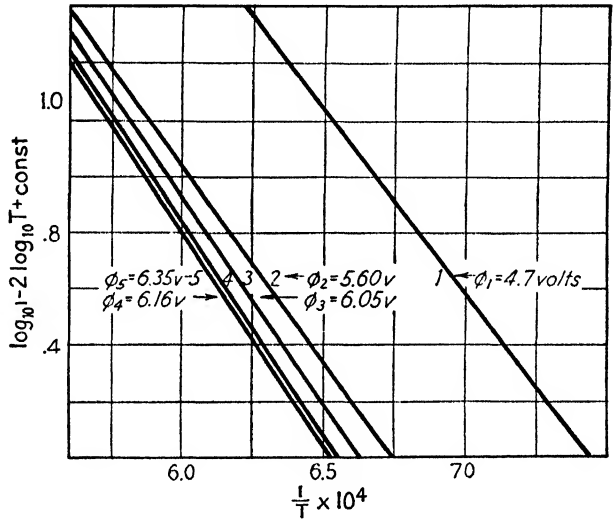

FIG. 3-14.—Thermionic curves for Pt during outgassing. 1. Before heating. 5. After 300 hr. of heating.

of the photoelectric work function, 6.30 volts, observed for the same specimen. Within the limits of error it was thus established that the photoelectric and thermionic work functions for clean platinum are identical.

Measurements were also made of the thermionic constant A, which is theoretically a universal constant having the value 60 amp/cm^2 deg^2. For clean platinum, however, the value of A came out to be 17,000. During the clean-up process, A was found to change in the same direction as ϕ_t and in such a way that log A is a linear function of ϕ_t. The interesting theoretical consequences of these results will be discussed in Sec. 6-14.

3-14. Effects of Various Gases.—The question as to which gases were chiefly responsible for the observed variations in the photoelectric properties of platinum has been extensively investigated. A systematic series of experiments was carried out by Welo,[1] who collected the gases

[1] L. A. WELO, *Phys. Rev.*, **12**, 251 (1918); *Phil. Mag.*, **45**, 593 (1923).

given out by the specimen during heating and examined them spectroscopically. He found in the case of platinum that the predominant spectra observed were those of hydrogen and carbon. The presence of the former is not surprising in view of the well-known affinity of platinum for it. The presence of carbon was ascribed to the organic vapors from wax and stop-cock grease. The observations indicated that both hydrogen and organic vapors tended to assist the photoelectric process (reduce the work function). Reintroducing them into the cell after the outgassing process did in fact cause the sensitivity again to increase.

The effect of hydrogen has been tried by many other observers and there is general agreement that the presence of this gas in the platinum surface tends to reduce the photoelectric work function (see Table 3-3, page 78). Thus Herrmann[1] found that heating a previously outgassed specimen in pure hydrogen at a pressure of 30 mm Hg caused in a short time a twenty-two fold increase in its sensitivity to the light from a mercury arc. Eichler[2] introduced hydrogen into platinum specimens by generating it electrolytically at the rear of the plate on which measurements were being made, and allowing it to diffuse through. It was found that shortly after starting the flow of gas there was a sudden large increase in the photoelectric sensitivity, presumably indicating a shift of the threshold toward the red.

The results of these and many other experiments[3] make it logical to conclude that the small values of the work function for fresh platinum are due to the presence of hydrogen in the surface, and it is only after extended treatment that the last traces of this gas can be removed and the true work function for the pure metal observed. It is possible that other gases, such as wax and water vapors, also contribute to the effect. Suhrmann[4] obtained evidence to show that hydrogen had a marked effect on photoelectric properties, only if it was ionized.

There is no general agreement as to the effects of oxygen. Herrmann and DuBridge have reported that its presence produced a decrease in photoelectric sensitivity while Eichler found an increased emission. In any case the effect is not as great as with hydrogen, and is probably greatly complicated by the presence of slight traces of more active gases and vapors present as impurities, and also by traces of gases not yet removed from the specimen itself. Ammonia vapor has been found to cause a marked shift of the threshold to the red.[5]

The effects of wax and grease vapors alone are not easy to observe, though it is recognized that they may be large. DuBridge notes that in

[1] *Loc. cit.*

[2] H. Eichler, *Zeits. f. Wiss. Photog.*, **16**, 10 (1916).

[3] See O. Rietschel, *Ann. d. Phys.*, **80**, 71 (1926).

[4] R. Suhrmann, *Phys. Zeits.*, **30**, 939 (1929).

[5] H. Leupold, *Ann. d. Phys.*, **82**, 841 (1927).

one case the removal of a side tube containing a hard wax joint caused an immediate increase of nearly 1 volt in the work function of the platinum specimen under test. Every effort has been made in recent years to eliminate such vapors from the tube entirely, since it is only then that thoroughly reliable results can be obtained.

The effect of gases, particularly hydrogen, on the *thermionic work function* of platinum has been studied in detail by Richardson,[1] H. A. Wilson,[2] and others with interesting results. They also find that the occlusion of this gas tends to decrease the work function, as well as the constant A. Wilson found that ϕ_t could be reduced to as low as 2.2 volts by heating in a hydrogen atmosphere. Lockrow[3] found the thermionic currents to be decreased slightly by O_2, or air, and increased by H_2. He concluded, however, that much of the observed increase was due to the presence of wax and oil vapors.

3-15. Thermionic and Photoelectric Properties of Tungsten.—The thermionic work function for tungsten has long been known with greater precision than for any other metal. The remarkable work of Langmuir[4] on this metal showed for the first time that it was possible to eliminate the effects of surface gas and obtain the thermionic current characteristic of the metal itself. The later well-known work of Dushman and his associates,[5] of Davisson and Germer,[6] and Zwikker[7] have yielded precise values of the work function which agree with each other within about 0.5 per cent. From their measurements it is possible to place the most probable value of this quantity with considerable certainty at 4.52 ± 0.02 volts. The precision with which this quantity is known for tungsten makes it possible to test very accurately for the cleanliness of a tungsten surface in vacuum by noting whether it exhibits the above value of ϕ_t. Tungsten is particularly well suited for thermionic measurements since, because of its high melting point, it is possible to obtain easily measurable currents over a range of temperature of 1500°C or more.

Only a few investigations of the photoelectric properties of tungsten have been reported. Hagenow[8] in 1919 made the first attempt to determine the photoelectric threshold under the best vacuum conditions. After long heat treatment the long wave limit was located at 2300A (5.36 volts). In view of later experiments, however, it seems evident that the treatment had not been sufficiently severe to remove oxide layers.

[1] O. W. Richardson, "Emission of Electricity from Hot Bodies," p. 118.
[2] H. A. Wilson, *Phil. Trans. Roy. Soc.*, **A208**, 251 (1908).
[3] L. Lockrow, *Phys. Rev.*, **19**, 97 (1922).
[4] I. Langmuir, *Phys. Rev.*, **2**, 450 (1913).
[5] S. Dushman, Rowe, Ewald, and Kidner, *Phys. Rev.*, **25**, 338 (1925).
[6] C. J. Davisson and L. H. Germer, *Phys. Rev.*, **20**, 300 (1922).
[7] C. Zwikker, *Proc. Amst. Acad. Sci.*, **29**, 792 (1926).
[8] C. F. Hagenow, *Phys. Rev.*, **13**, 415 (1919).

More recently Roy[1] and Harrison[2] have reported values of 2735 and 2700A (4.5 volts) for the threshold, though in neither case were completely gas-free conditions obtained.

A systematic study of the photoelectric properties of tungsten was made by Warner[3] in 1927. A diagram of his apparatus is shown in Fig. 3-15. The specimen consisted of a filament T of tungsten wire wound in a conical spiral which presented a fairly large area to the incident light. It was surrounded by a collecting cylinder C, of platinum, which could be heated by means of an induction furnace. All wax joints were eliminated from the high vacuum side of the pumps and it was found that the most consistent results were obtained by sealing off the tube from the pumps after a thorough initial outgassing, completing the clean-up by the use of vaporized magnesium. During the first part of the outgassing it was found that the thermionic work function was greater at low temperatures than at high. This could be interpreted as due to the formation of the inactive oxide on the cool surface. (Kingdon[4] has found that a surface of oxidized tungsten has a thermionic work function of 9.0 volts.) After long heating at temperatures above 2500°K this effect disappeared and the work function was constant at all temperatures, and in agreement with the values obtained by other observers. The value of the photoelectric threshold obtained from spectral distribution curves was 2570A and was independent of the temperature. The corresponding work function, 4.79 volts, is somewhat higher than the thermionic value, 4.52 volts, obtained by using the usual Richardson T^2 law, but is in good agreement with the value, 4.72 volts, obtained by Davisson and Germer from the $T^{\frac{1}{2}}$ equation. Theoretically the agreement should be with the value obtained from the T^2 relation, and Warner in later experiments has in fact found the threshold of an evaporated tungsten layer to be at 2650A (4.58 volts).

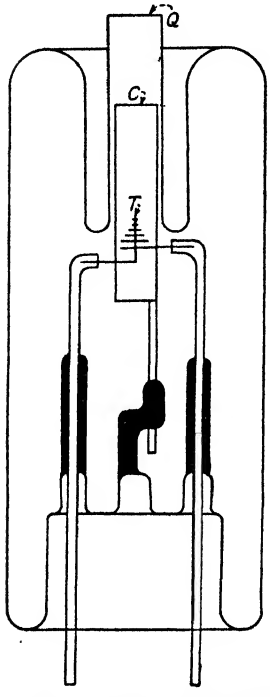

FIG. 3-15.—Apparatus for study of photoelectric and thermionic work functions of tungsten. (*Warner.*)

The behavior of the threshold for tungsten during outgassing is quite different from that of platinum. A fresh specimen of tungsten was found

[1] S. C. ROY, *Proc. Roy. Soc.*, **112**, 599 (1926).

[2] T. H. HARRISON, *Proc. Phys. Soc. Lond.*, **38**, 214 (1926).

[3] A. H. WARNER, *Proc. Nat. Acad. Sci.*, **13**, 56 (1927); *Phys. Rev.*, **33**, 815 (1929); **37**, 233 (1931).

[4] K. H. KINGDON, *Phys. Rev.*, **24**, 510 (1924).

by Warner to be completely insensitive to the radiation from the mercury arc. During the heating of the specimen the limit shifts steadily to the *longer* wave-lengths reaching finally the limiting value 2570A. In view of the results of Kingdon already mentioned, it seems probable that the outgassing process consists mainly in the removal of a film of the inactive oxide from the surface. The oxide film gives rise to another interesting effect observed by Warner. It was found that, while the photoelectric *threshold* was independent of temperature, the photocurrent excited

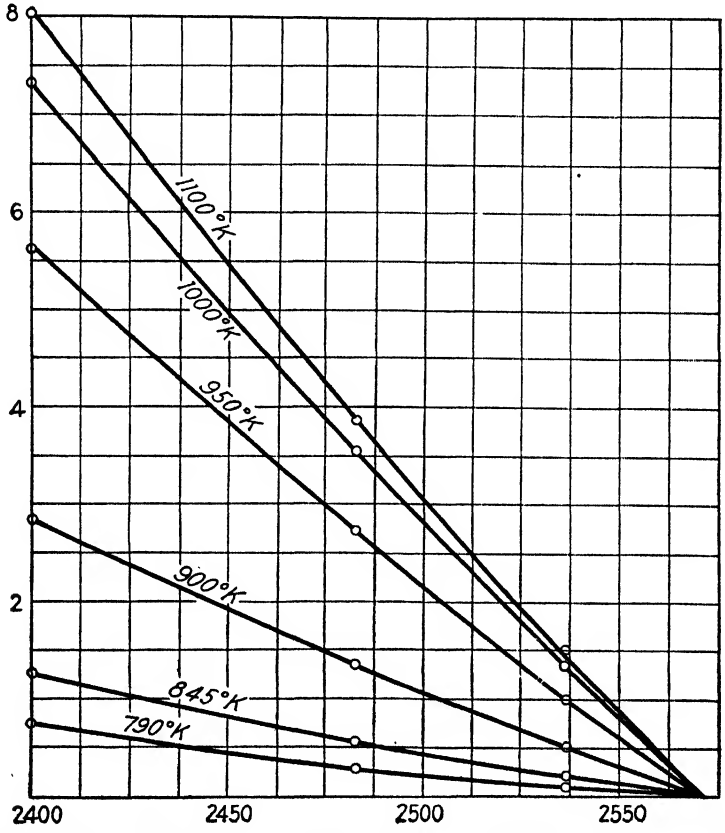

FIG. 3-16.—Spectral distribution curves for outgassed tungsten at various temperatures.

by light of a given frequency on the short-wave side of the threshold was not constant but increased rapidly with rising temperature up to nearly 1100°K, at which point it approached a constant value. A series of curves obtained at different temperatures is shown in Fig. 3-16. The curves can be explained by assuming that at the lower temperatures a larger fraction of the surface is covered by the oxide layer, rendering it insensitive. At all temperatures, however, a portion of the clean surface is left exposed from which the electron emission is measured, and for which, of course, the threshold is constant.

No studies of the effects of other gases on the photoelectric effect from tungsten seem to have been made. Langmuir[1] has studied their effect on the thermionic work function, however, and found that it is considerably increased by the presence of hydrogen, oxygen, nitrogen, carbon monoxide and carbon dioxide. The effects did not depend in a regular way on the pressure, however, and Langmuir was inclined to attribute the effects of hydrogen and nitrogen to the presence of traces of water vapor and oxygen introduced with them, or released by their chemical action.[2,3]

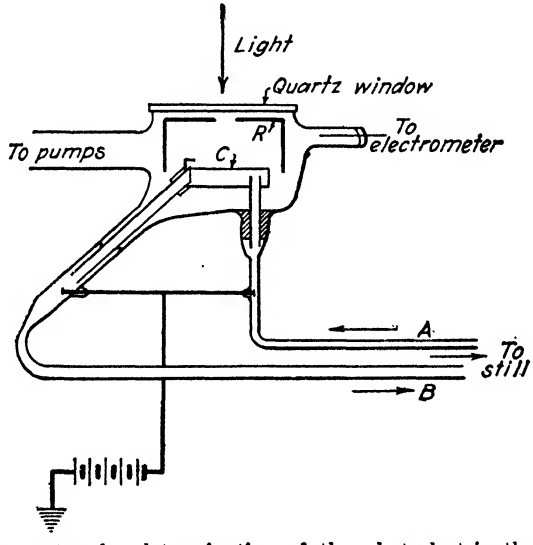

FIG. 3-17.—Apparatus for determination of the photoelectric threshold of flowing mercury. (*Kazda.*) *A.* Glass inlet tube from still. *B.* Glass return tube. *C.* Iron cup, with inlet and overflow tubes of iron. *R.* Copper oxide receiving cylinder.

3-16. Threshold of Clean Mercury.—Liquid mercury surfaces were first studied by Pohl and Pringsheim[4] in 1913, who reported a value for the threshold in the neighborhood of 2600A. Derieux[5] and Taubes[6] determined the threshold for minute droplets of mercury in a Millikan condenser, each finding values in the region near 3000A. No attempt was made, however, to secure gas-free surfaces. In 1925 Kazda[7] reported on an elaborate experiment in which the effects of gases were eliminated by the scheme which had been previously tried by Hughes[8] of making measurements on a flowing surface of the freshly distilled metal. A

[1] I. LANGMUIR, *Jour. Amer. Chem. Soc.*, **38**, 2221 (1916).
[2] I. LANGMUIR, *Phys. Rev.*, **37**, 1006 (1931).
[3] S. DUSHMAN, *Rev. Mod. Phys.*, **2**, 446 (1930).
[4] R. POHL and P. PRINGSHEIM, *Verh. d. Deutsch. Phys. Ges.*, **15**, 111 (1913).
[5] J. B. DERIEUX, *Phys. Rev.*, **11**, 276 (1918).
[6] S. TAUBES, *Ann. d. Phys.*, **76**, 629 (1925).
[7] C. B. KAZDA, *Phys. Rev.*, **26**, 643 (1925).
[8] A. L. HUGHES, *Phil. Trans. Roy. Soc.*, **A212**, 205 (1912).

sketch of Kazda's apparatus is reproduced in Fig. 3-17. Clean mercury was evaporated in a high-vacuum still and on condensation in the condenser ran through a tube A into the cup C, where its surface was exposed to monochromatic radiation admitted through a quartz window directly above. The photocurrents to the collecting cylinder R were measured by means of an electrometer. When the cup was filled the mercury flowed over the edge and ran back to the still, so that measurements were made on a continually flowing surface. It was calculated from the rate of flow that the average molecule did not remain on the surface for more than a few seconds—a time too short to allow the surface to become contaminated by residual gases in the tube. Troublesome elec-

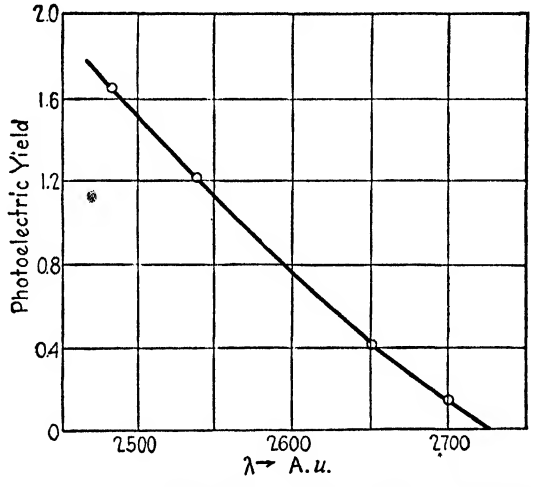

FIG. 3-18.—Spectral distribution curve for clean, flowing mercury.

trostatic effects could be eliminated only by the most careful shielding of all glass parts in which frictional charges could be generated by the flow. A careful measurement was made of the relative intensities of the lines in the mercury spectrum through the use of a sensitive vacuum thermopile. The long wave limit for the flowing surface appeared consistently at 2735A, as determined from the spectral distribution curve shown in Fig. 3-18. When the flow was stopped, however, it shifted at once to longer wave-lengths.

The cause of this shift has been investigated by Dunn[1] and Hales,[2] who rebuilt the apparatus used by Kazda, making some improvements. Kazda and Dunn found that the shift was accelerated when the liquid air was removed from the trap, thereby concluding that condensible vapors were responsible for the effect. Hales in rebuilding the apparatus eliminated all wax and grease joints and found that the shift disappeared,

[1] H. K. DUNN, *Phys. Rev.*, **29**, 693 (1927).
[2] W. B. HALES, *Phys. Rev.*, **32**, 950 (1928).

so that the threshold for the stationary and flowing surfaces was the same, namely, 2735A.

To determine whether other gases had an effect on the emission, hydrogen was introduced into the cell so that it was in contact with the stationary surface. There was no effect on the threshold. Hydrogen admitted to the *still*, similarly had no effect if conditions were such that the surface was thoroughly clean. If, however, the illuminated surface was already contaminated by other impurities the effect of introducing hydrogen into the still—even though it was not operating and the mercury at rest—was to counteract the effect of the impurity. It was concluded that the hydrogen must diffuse directly through the mercury column *A* (Fig. 3-17) which was 30 cm long and 0.5 cm in diameter, the time required being of the order of only a few minutes. Such a diffusion of gas directly into the body of metals would explain much of the difficulty in securing gas-free surfaces.

Hales tried the effect of other gases on the stationary surface. N_2, A, and He were found to have no effect. Small amounts of water vapor decreased the sensitivity for the various incident wave-lengths but left the threshold unchanged. Larger amounts of water vapor shifted the limit to the red. Oxygen caused a shift in the limit toward the shorter wave-lengths, from 2735A to 2555A.

3-17. Other Metals. 1. *Tin.*—An elaborate study of the photoelectric threshold of tin has been made by Goetz.[1] His primary object was to study possible changes in the threshold at the melting and transition points, and his experimental technique will be described more in detail under this heading in Sec. **3-30**. It will be sufficient to point out here that after taking elaborate precautions to obtain a pure, gas-free surface, reliable threshold measurements using monochromatic light were made on the two crystal modifications of solid tin and on liquid tin. The values characteristic of the β, γ, and liquid forms are respectively, 2740A, 2820A, and 2925A. Great difficulty was encountered in removing the last traces of oxide, and this was finally accomplished by extended heating of the liquefied metal under a stream of very pure hydrogen, followed by heating in vacuum. Oxidized tin was quite insensitive to light from the quartz mercury arc.

2. *Iron.*—Using the general outgassing methods and vacuum technique described by DuBridge, other observers, working at the University of Wisconsin Laboratories under the direction of Mendenhall, have recently made studies of the thermionic and photoelectric properties of Fe, Co, Mo, Rh, Ag, Au, Zn, and Ta. In each case it was found that after long heat treatment the photoelectric threshold approached a final value which was not changed by further outgassing. In each case also

[1] A. Goetz, *Phys. Rev.*, **33**, 373 (1929).

interesting variations of the photoelectric effect with temperature were found, and these will be discussed in Sec. **3-26.**

Cardwell[1] has reported the results of a study of iron, in which it was found that during heat treatment the photoelectric sensitivity of this metal to the total radiation from a quartz mercury arc showed first a sharp increase, then a rapid decrease to a minimum value, and finally a slower rise to a final limiting value (Fig. 3-19). In one case the final value was reached only after 120 hr of heating at temperatures up to 900°C, and then was not changed by nearly 100 hr of additional heating. The photoelectric threshold of the outgassed specimen was located by means of filters to be between the mercury lines 2580A and 2652A, corresponding to a work function of 4.72 ± 0.07 volts.

It was found that the sensitivity of the specimen is considerably smaller when it is cooled *suddenly* than when cooled *slowly* from a temperature above 910°C (at which the transition from the β- to γ-crystal form takes place). This was attributed to the fact that part of the γ-form is retained by the quickly cooled specimen and this has a larger work function. The *threshold* was the same, however, for the supercooled specimen, as would be expected, since the threshold for a mixture of crystals would be that of the most sensitive form.

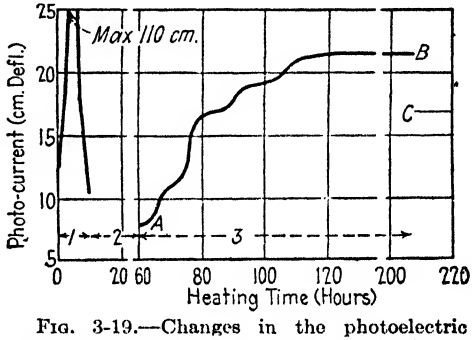

FIG. 3-19.—Changes in the photoelectric sensitivity of iron during outgassing. (*Cardwell.*) Interval 1 (0 to 10 hr), heated filament at 300°C. Interval 2 (10 to 60 hr), baked entire tube at 550°C. Interval 3 (60 to 206 hr), glowed filament at 875°C. Sensitivity drops to value indicated by *C* when metal is cooled suddenly from above 910°C.

The photoelectric and thermionic properties of outgassed cobalt as affected by changes in crystal structure have also been studied by Cardwell,[2] but values for the threshold were not given.[3] The total sensitivity to the mercury-arc radiation was found to increase to a constant value as the outgassing progressed.

3. *Molybdenum.*—For this metal Martin[4] found that the photoelectric threshold, as determined by means of light filters, shifted from the value 2600A for a fresh specimen to a final value of 3800A, attained after 300 hr of heating. The latter value corresponds to a work function of 3.22 volts, with the uncertainty given as ±0.16 volt. For the same specimen

[1] A. B. CARDWELL, *Proc. Nat. Acad. Sci.*, **14**, 439 (1928).

[2] A. B. CARDWELL, *Proc. Nat. Acad. Sci.*, **15**, 544 (1929).

[3] Dr. Cardwell has recently informed the authors that he has found the work functions of outgassed Cobalt to be 4.25 ± 0.08 volts and 4.12 ± 0.04 volts for the hexagonal and face-centered cubic forms, respectively.

[4] M. J. MARTIN, *Phys. Rev.*, **33**, 991 (1929).

the thermionic work function, determined from the slope of a Richardson plot, came out 3.48 ± 0.07 volts. This is somewhat higher than the photoelectric value but there was observed an increase in the photoelectric work function with rise in temperature, so that at high temperatures it would approach the thermionic value. While these results show that the photoelectric and thermionic work functions are in fair agreement for the specimen studied, they may not represent the value for thoroughly cleaned molybdenum, since they are considerably lower than the value, 4.41 volts, obtained by careful measurements of Dushman and his co-workers.[1] Dushman found that electropositive impurities could be removed from molybdenum only by extended heating at temperatures above 2500°K, while the highest temperature used by Martin was of the order of 1800°K.

4. *Rhodium.*—Quite recently an extended study of the photoelectric and thermionic work functions of rhodium has been reported by Dixon,[2] using the same general experimental technique. The photoelectric threshold (determined by means of filters) was found to shift from an initial value of about 2400A for a fresh specimen up to a maximum at 2967A after 25 hr heating, and then back to a final value lying between the mercury lines 2482A and 2536A. This final value was reached only after 676 hr of heating at temperatures up to 1250°C and in a pressure of 10^{-7} to 10^{-8} mm Hg. The limit was not further changed by an *additional* 280 hr of heating at 1450°C (1056 hr, or about 6 weeks, in all!). The corresponding work function is 4.92 ± 0.06 volts.

Observing the photoelectric sensitivity as a function of temperature, it was noted that a sudden change took place at approximately 513°K, due apparently to a change in crystal structure. The long wave limit was shifted to a value between 2652A and 2752A, giving a work function at this temperature of 4.57 ± 0.09 volts. There was no further shift in the limit up to at least 920°K, though the total sensitivity showed a steady increase between 513 and 920°K.

The thermionic work function of the outgassed rhodium was determined by measuring the emission over a range of temperatures from about 1350 to 1500°K, the slope of the Richardson plot giving $\phi_t = 4.58$ volts. This is in excellent agreement with the photoelectric value determined at 513°K.

Introducing pure hydrogen into the cell after the outgassing caused the threshold to shift about 50A to 100A to the violet, while the introduction of oxygen shifted the threshold to below 2300A, the limit of measurements. In each case the threshold was restored to the value characteristic of the outgassed rhodium by heating for 100 hr at 1000°C in vacuum.

[1] S. Dushman *et al.*, *Phys. Rev.*, **25**, 338 (1925).
[2] E. H. Dixon, *Phys. Rev.*, **37**, 60 (1930).

5. *Silver.*—An extensive study of this metal, recently reported by Winch,[1] shows that the threshold shifts from a value near 2000A for a fresh specimen up to a value above 3300A after 400 hr of heating at temperatures up to 325°C. Further heating at temperatures up to 600°C causes the threshold wave-length to shift back to 2610A after a total of 800 hr of heating, and 400 hr of additional heating at this temperature with occasional "flashing" at 850°C (where rapid vaporization took place) produced no further change in the limit. The work function of the clean specimen is thus given as 4.73 ± 0.07 volts. When the photocurrent was taken with the filament hot, the threshold was found to shift to the red, reaching the value 2700A at 600°C, corresponding to a work function at this temperature of 4.56 ± 0.06 volts.

6. *Gold.*—Morris[2] has reported changes in the photoelectric sensitivity of gold during outgassing quite similar to those observed for silver, except that the final value reached after 1800 hr (!) of heating at 650°C was found to be 2560A (4.82 volts) when measured at room temperature. With increasing temperature the threshold of the clean specimen shifted to 2610A (4.73 volts) at 720°C.

7. *Zinc* has been used in many photoelectric experiments and is often employed in certain types of photoelectric cells because of its sensitivity to ordinary sunlight. The threshold has been found by various observers to be between 3000A and 4000A, though the value for the clean metal is not precisely known. It is well known that in air a freshly scraped zinc plate rapidly loses its photoelectric sensitivity. In 1914 Küstner[3] carried out an extensive series of tests on zinc surfaces which were repeatedly scraped in high vacuum to remove surface layers. It was found that large photoelectric currents were obtained immediately after repeated scraping, and these often decreased with time. In some cases, after a glow discharge had been passed, the currents disappeared and Küstner therefore concluded that gas-free zinc would be photoelectrically inactive. This conclusion seems scarcely warranted by his own experimental curves.

Quite recently Mendenhall and Dillon[4] have studied the photoelectric properties of single-crystal zinc under much better vacuum conditions than have previously been used, and they find no evidence to support Küstner's conclusion. In their experiments the zinc was melted and outgassed in high vacuum, then crystallized and transferred to the photoelectric cell, where it was given further outgassing treatment. In its most gas-free state the zinc single crystals exhibited a threshold in the

[1] R. P. Winch, *Phys. Rev.*, **37**, 1269 (1931).

[2] L. W. Morris, *Phys. Rev.*, **37**, 1263 (1931).

[3] H. Küstner, *Phys. Zeits.*, **15**, 58 (1914); *Ann. d. Phys.*, **46**, 893 (1915).

[4] C. E. Mendenhall and J. H. Dillon, private communication. J .H. Dillon, *Phys. Rev.*, **38**, 408 (1931).

neighborhood of 3460A. The polycrystalline surface showed a threshold near 3720A. It was found that the photoelectric currents in some cases changed spontaneously during exposure to ultra-violet light, and it was concluded that the light actually assisted in removing gas from the surface. Long exposure to light caused the threshold to approach the steady value given above.

8. *Palladium.*—The effects of gas particularly hydrogen, on the photoelectric sensitivity of palladium have been studied by Eichler,[1] Stumpf,[2] Dümpelmann and Hein,[3] and DuBridge and Roehr.[4] All have reported very large increases in the photoelectric effect due to the presence of hydrogen. An investigation of a series of Pd-Ag alloys having different

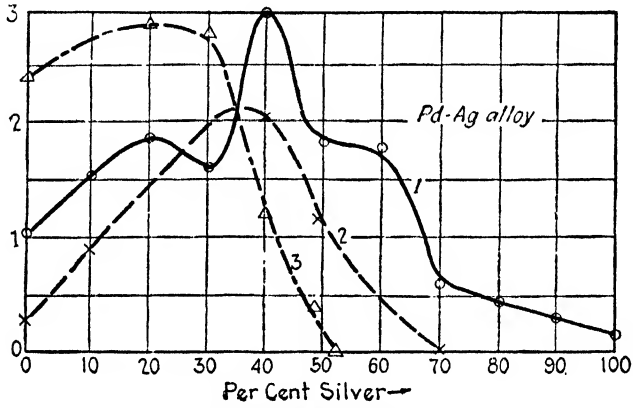

FIG. 3-20.—Photo-current and gas absorption of Pd-Ag alloys. 1. Photoelectric current. (*Krüger and Ehmer.*) 2. Absorption of H_2. (*Sieverts.*) 3. Electrolytic absorption of H_2. (*Nowack.*)

capacities for absorbing this gas was carried out by Krüger and Ehmer.[5] They plotted the photoelectric sensitivity of the specimen as a function of the silver content, obtaining curve 1, shown in Fig. 3-20. It will be seen that there is a maximum at about 40 per cent silver. The data obtained by Sieverts[6] on the amount of hydrogen absorbed by these alloys are shown in curve 2, and it will be noted that it reaches a maximum also at approximately 40 per cent silver. The more recent data of Nowack[7] show, however, that the maximum is nearer 20 per cent silver (curve 3). The experiments are illustrative, nevertheless, of the close connection between the photoelectric properties and the gas content of a

[1] H. EICHLER, *Zeits. f. Wiss. Photog.*, **16**, 10 (1916).
[2] F. STUMPF, *Verh. d. Deutsch. Phys. Ges.*, **16**, 989 (1914).
[3] R. DÜMPELMANN and W. HEIN, *Zeits. f. Phys.*, **22**, 368 (1924).
[4] L. A. DUBRIDGE and W. W. ROEHR, *Phys. Rev.*, **39**, 99 (1932).
[5] F. KRÜGER and A. EHMER, *Zeits. f. Phys.*, **14**, 1 (1923).
[6] A. SIEVERTS, *Zeits. f. Anorgan. Chem.*, **92**, 329 (1915).
[7] NOWACK, *Zeit. f. Anorgan. Chem.*, **113**, 1 (1920). See "International Critical Tables," Vol. III, p. 253.

surface. The photoelectric threshold for pure outgassed palladium is probably in the neighborhood of 2488A (4.96 volts).[1]

9. *Tantalum.*—The threshold for pure tantalum after over 900 hr of heat treatment in vacuum was found by Cardwell[2] to be in the neighborhood of 3050A for a temperature of 700°C. The outgassing temperatures employed were as high as 2600°C. The value of the work function at room temperature is thus 4.05 volts, in good agreement with the value 4.07 volts for the thermionic work function obtained by Dushman.

3-18. The Alkali Metals.—The metals discussed in the previous sections are the only ones for which the photoelectric thresholds have been measured with precision under extremely gas-free conditions. The alkali metals, however, have had their photoelectric properties very extensively studied, and while there is some disagreement as to the precise values of the thresholds, nevertheless some of the most important advances in the study of the nature of the photoelectric process and the most precise tests of the fundamental laws of photoelectricity have been made with surfaces of these metals. For this reason their properties will be discussed in some detail.

As we have seen in the previous chapter, the alkali metals have the great advantage that their thresholds are in the visible spectrum, so that there is a wide range of available wave-lengths for which the surfaces are active. Hence very large photocurrents can be obtained with ordinary sources of light without the necessity of using quartz windows and optical systems. For these reasons, sodium, potassium, and caesium, in particular, have found a wide use in commercial photoelectric cells.

The earliest studies of these metals led to directly conflicting results. Wiedmann and Hallwachs[3] and Fredenhagen[4] found that repeated distillation of potassium in vacuum caused the photocurrents excited by light of wave-length longer than 3300A to fall to less than 1 per cent of the initial value. But Pohl and Pringsheim[5] found that continued boiling in vacuum, until all measurable evolution of gas had ceased, caused no change in the currents for wave-lengths longer than 4360A. The careful experiments of Elster and Geitel[6] and of Ives, Dushman, and Karrer[7] also showed that multiple distillation of potassium in high vacuum produced almost no change in its photoelectric properties. They still obtained large currents with visible light, and were able to find evidence that the results of Wiedmann and Hallwachs were spurious.

[1] L. A. DuBridge and W. W. Roehr, *loc. cit.*

[2] A. B. Cardwell, *Phys. Rev.*, **38**, 2041 (1931).

[3] G. Wiedmann and W. Hallwachs, *Verh. d. Deutsch. Phys. Ges.*, **16**, 107 (1914); G. Wiedmann, *ibid.*, **17**, 343 (1914).

[4] K. Fredenhagen, *Phys. Zeits.*, **15**, 65 (1914).

[5] R. Pohl and P. Pringsheim, *Verh. d. Deutsch. Phys. Ges.*, **16**, 336 (1914).

[6] J. Elster and H. Geitel, *Phys. Zeits.*, **11**, 260 (1910).

[7] H. E. Ives, S. Dushman, and E. Karrer, *Astrophys. Jour.*, **43**, 9 (1916).

Millikan and Souder[1] studied the thresholds for surfaces of alkali metals which had been freshly cut in vacuum and found them in every case to be at wave-lengths greater than 5000A. There was thus convincing evidence that the photoelectric sensitivity of the alkali metals to visible light did not depend on the presence of gas layers, a conclusion which has been repeatedly confirmed by more recent work.

The technique of handling and of outgassing the alkali metals is of course quite different from that used for the more refractory metals.[2] The metals are introduced into the vacuum either in the form of pieces of the pure metal, always heavily oxidized, or in the form of a chemical compound which can be broken down by heating. By successive distillation under good vacuum conditions they may, however, be finally brought into the experimental tube in a fairly gas-free state. And if vacuum conditions are maintained sufficiently good in the tube, the surface will retain a constant photoelectric sensitivity for long periods of time. Burt[3] has obtained clean sodium surfaces by electrolysis of the metal directly through the glass walls of an evacuated cell.

In spite of the fact that the alkali metals have been widely used in photoelectric studies, there are but few reliable published values of their thresholds. This is due to several factors. In the first place these thresholds seem to be excessively sensitive to the type of surface employed. For example, Ives and Johnsrud[4] found the following values for the threshold of pure potassium under various conditions, all fairly gas-free:

Matte surface	6100A
Molten pool	6000A
Specular layer on glass	5200A
Thin film on Pt	5100A

Other observers with still different surface conditions have obtained other values, and it is difficult to decide whether there is any single value which can be said to be characteristic of the potassium itself.

In the second place there is evidence[5] that the thresholds for the alkali metals are not as sharp as for some of the other metals, so that the values of the threshold obtained will depend on the sensitivity of the measuring instrument used. The actual intercept of the spectral distribution curve may be uncertain to within 200A or more.

Finally, the alkali metals are even more sensitive than others to the presence of slight traces of gas, particularly hydrogen and oxygen. The effect of the former is illustrated by the well-known process of sensitization of potassium surfaces by a glow discharge in hydrogen which may

[1] R. A. Millikan and W. H. Souder, *Phys. Rev.*, **4**, 73 (1914).

[2] See Chap. XII for further details.

[3] R. C. Burt, *Phil. Mag.*, **49**, 1158 (1925).

[4] H. E. Ives and A. L. Johnsrud, *Astrophys. Jour.*, **60**, 231 (1924).

[5] H. E. Ives, *Jour. Opt. Soc. Amer.*, **8**, 551 (1924); J. W. Hornbeck, *Phys. Rev.*, **24**, 631 (1924).

shift the threshold to the red as much as 3000A. Because of their great affinity for these gases their elimination from alkali-metal cells is an almost impossible task, even when the best vacuum technique is employed.

The first threshold measurements for alkali metals distilled in vacuum were made by Pohl and Pringsheim who obtained values in good agreement with those obtained in more recent work. Millikan[1] determined the thresholds of surfaces freshly cut in vacuum, using the stopping potential method. While such surfaces showed quite consistent behavior if measurements were made immediately after cutting, it is not to be expected, of course, that they are gas *free*, since the alkali metals undoubtedly contain large quantities of *absorbed* gases. Measurements on distilled alkali metals have also been made by Miss Seiler.[2] While the measurements were made in cells filled with argon, it has been shown by Wiedmann and Hallwachs[3] that the presence of this gas has no appreciable effect on the photoelectric emission from potassium. Her measurements[4] can possibly be taken as representing fairly well the thresholds for these metals as they are ordinarily used. According to A. R. Olpin[5] the most reliable and reproducible values of the thresholds of the alkali metals are obtained when thin films of the metal are allowed to deposit spontaneously at room temperature on the carefully outgassed surfaces of polished metal plates, all under extremely high vacuum conditions. As such films build up, the threshold shifts first to the red and then back toward a limiting value as the film reaches its equilibrium thickness,[6] which is probably of the order of several atomic layers. The values of the thresholds so obtained are listed under Column III of Table 3-2, page 75.

3-19. Double Thresholds.—An interesting phenomenon discovered by Richardson and Young[7] may help to account for some of the lack of agreement in measurements of alkali-metal thresholds. These authors have found that under certain conditions sodium or potassium surfaces may have *two* thresholds. The evidence for this may be understood by reference to the curves of Fig. 3-21, which are typical of those obtained for K. Curve I was obtained for a thoroughly outgassed surface and is a usual type of spectral distribution curve with a maximum at 4400A and a threshold intercept at 7000A. (Tests with filters showed that the rather pronounced "foot" was not due to scattered light.) If the surface is now sensitized by admitting pure hydrogen and passing an electrical discharge, the photocurrents are greatly changed and a curve of the type II is obtained, containing maxima at 4400A and 6000A. Similar curves had been obtained some years previously by Richardson and Compton.[8] Now

[1] R. A. Millikan, *Phys. Rev.*, **7**, 355 (1916).
[2] E. F. Seiler, *Astrophys. Jour.*, **50**, 129 (1920).
[3] G. Wiedmann and W. Hallwachs, *Verh. d. Deutsch. Phys. Ges.*, **16**, 107 (1914).
[4] See Fig. 12-8, p. 424.
[5] A. R. Olpin, private communication.
[6] H. E. Ives and A. R. Olpin, *Phys. Rev.*, **34**, 117 (1929).
[7] O. W. Richardson and A. F. A. Young, *Proc. Roy. Soc.*, **107**, 377 (1925); A. F. A. Young, *Proc. Roy. Soc.*, **104**, 611 (1923).
[8] O. W. Richardson and K. T. Compton, *Phil. Mag.*, **26**, 549 (1913).

Richardson[1] had predicted from his theory that a metal surface with a threshold, say ν_0, would have a maximum photoelectric yield at a frequency $(\frac{3}{2})\nu_0$. The threshold at 7000A and the maximum at 4400A satisfy this condition. The presence of two maxima then suggested the existence of a double threshold, the new maximum at 6000A leading to a predicted threshold at 10,000A. By extending their measurements into the infra-red, evidence of a threshold at this value was indeed found. The two thresholds correspond to work functions of 1.77 and 1.24 volts.

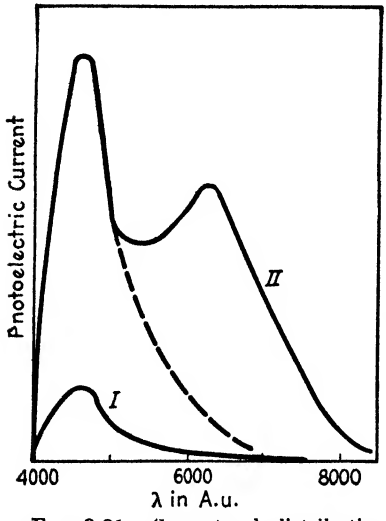

FIG. 3-21.—Spectral distribution curves for clean (I) and sensitized (II) potassium, the latter showing a double threshold. (*Richardson and Young.*)

To explain the double threshold it was suggested that the surface must have been covered with minute patches of contamination, caused by the H_2 discharge, which have a lower work function than the clean portions of the surface. If the total area of these patches was relatively small, their presence would in fact be expected to give rise to a curve similar to those obtained.

Richardson and Young have also obtained evidence for the existence of a double thermionic work function for a sensitized potassium surface, though there is a lack of quantitative agreement between the photoelectric and thermionic values. A typical thermionic curve obtained for sensitized K is shown in Fig. 3-22. It will be noted that the curve instead of being a straight line is convex toward the origin, though it becomes asymptotic to straight lines at low and high temperatures. The slopes of these lines give work functions of 1.1 and 0.4 volt. Such a curve can be interpreted if it is again assumed that the surface is composed of patches having different work functions, but it could also be ascribed to changes with temperature in the nature of the surface. Results similar to these have recently been obtained by Laird[2] under somewhat more carefully controlled conditions. He found $\phi_t = 0.26$ volt at 100°C and $\phi_t = 1.3$ volts over the range of 150 to 200°C for a clean potassium surface treated with hydrogen.

More recently the work has been continued in Richardson's laboratory by Miss Butterworth,[3] who has deduced the values of the photoelectric work function from measurements of the "complete" photoelectric emission by the method used by Roy described in Sec. 3-6. The values of the work function are given as 1.76 and 0.58 volts, corresponding to long-wave limits at 7100A and 21,000A, respectively. The agreement with the pairs of values obtained from the thermionic measurements and from the previous photoelectric measurements is not good—yet it is of interest that all three sets of experiments point definitely to the existence of two work functions for the same surface. Similar results are obtained for sodium surfaces which are properly sensitized. The evidence is in favor of a single threshold for all *clean* surfaces.

3-20. Effects of Gases on the Alkali Metals.—In studying the effects of gases on the photoelectric properties of the alkali metals most of the

[1] O. W. RICHARDSON, *Phil. Mag.*, **24**, 570 (1912). See Sec. 6-10.
[2] H. R. LAIRD, *Phys. Rev.*, **34**, 463 (1929).
[3] J. BUTTERWORTH, *Phil. Mag.*, **6**, 1 (1928).

interest has been centered on their effects on the "selective" photoelectric emission which will be discussed in Chapter V. It has been found that the presence of gas layers produces marked changes in the appearance of the spectral distribution curves for polarized light. Some of these investigations throw some light also on the effects of gases on the thresholds of the alkali metals, and of particular interest in this connection are two recent papers by Suhrmann[1] and Suhrmann and Theissing.[2] Using a high-vacuum photoelectric cell, these observers found that the

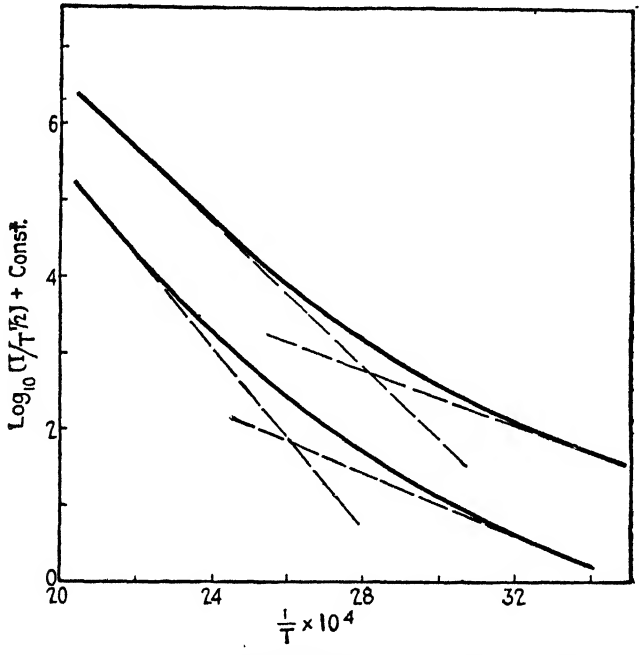

FIG. 3-22.—Thermionic curves for sensitized potassium showing "double" work function. (*Young.*)

threshold for a freshly distilled layer of potassium on a silver plate is approximately 5800A. This value is unchanged if pure hydrogen is introduced into the cell, but if the hydrogen is ionized in any way the threshold is shifted to 6400A. This is an important result, for the possibility of the gases being ionized has not been considered in most experimental studies of their effects on photoelectric thresholds.

However, Fleischer and Teichmann,[3] and Campbell[4] have concluded from a further study of this effect that ionization of the hydrogen does not play an important rôle, but that the threshold shift is due to hydrogen

[1] R. SUHRMANN, *Phys. Zeits.*, **29**, 811 (1928).
[2] R. SUHRMANN and H. THEISSING, *Zeits. f. Phys.*, **52**, 453 (1928).
[3] R. FLEISCHER and H. TEICHMANN, *Zeits. f. Phys.*, 61, 227 (1930).
[4] N. R. CAMPBELL, *Phys. Zeits.*, **30**, 320 (1929).

being in contact with the *vapor* of potassium in the tube thus forming a layer of some sort of potassium hydride on the surface.

3-21. Summary of Threshold Measurements.—The only metals which have been discussed in the preceding sections are those for which some attempt has been made to determine the threshold under gas-free conditions. To conserve space the other metals will not be discussed in detail, but all reported values of the thresholds of *all* the metals have been collected for reference in Table 3-2. In Column I of this table are listed the values of the thresholds which have been reported for surfaces which were not given outgassing treatment after being introduced into the vacuum. The preliminary treatment given varied widely in different experiments, though it usually involved merely mechanical cleaning, scraping, sand-papering, or polishing.

In Column II are listed the thresholds obtained for surfaces which were given some form of vacuum treatment. In some cases the surfaces were freshly cut or scraped while in vacuum just before the measurements. In the case of the easily vaporized metals the measurements were often made on freshly vacuum-distilled surfaces. For the higher melting-point metals some form of heat treatment was usually given.

In Column III are listed only the values obtained in recent years for surfaces which had been very thoroughly denuded of gases by the most drastic treatment in the highest vacua now attainable. They are in each case the *reproducible limiting values* which are not changed by further treatment, and hence they can be regarded as close to the thresholds characteristic of the pure gas-free metals. Those printed in **bold-face** type are thought to be particularly reliable.

In the last two columns are given the photoelectric and thermionic work functions expressed in volts. The former are calculated from the thresholds given in the previous columns. Values in parentheses are uncertain and those in **bold-face** type are in each case the most reliable values for thoroughly degassed surfaces. Only the best values for the thermionic work functions, as listed by Dushman,[1] have been included.

It will be noted that there are only three metals (Pt, Rh, and W) for which reliable measurements of both the thermionic and photoelectric work functions have been made for the same specimen. In these three cases there is very good agreement between the values. In many other cases the best thermionic value falls well within the range of the various photoelectric determinations. In the case of silver and gold the photoelectric work functions observed by Winch and Morris are considerably higher than the thermionic values reported by Goetz. Since the work function was found to increase with long outgassing treatment, one is inclined to believe the higher values represent the more gas-free state. There is still some question, however, as to the theoretical relation

[1] S. Dushman, *Rev. Mod. Phys.*, **2**, 381 (1930).

between photoelectric and thermionic work functions when they depend on the temperature of the surface, as with Ag and Au. It is probable that in this case they should *not* be exactly equal (Chapter VI).

TABLE 3-2.—PHOTOELECTRIC AND THERMIONIC WORK FUNCTIONS OF THE METALS

Metal	Threshold wave-length (A.u.)			ϕ Photoelectric, volts	ϕ Thermionic, volts
	I	II	III		
	No outgassing	Partial outgassing	Extended outgassing		
Ag	3213 [35] 3250 [14] 3364 [39] 3390 [22]	2888 [29] 3150 [8]	**2610** [53] (20°C) **2700** [53] (600°C)	**4.73** **4.56**	**4.08** [38] (925°C)
Al	3460 [35] 3595 [22] 3650 [45] 4132 [39] 4770 [3] 5000 [7]	3652 [11]		(2.5 to 3.6)	
Au	2625 [35]	2630 [29] 2850 [8]	**2650** [54] (20°C) **2610** [54] (740°C)	**4.82** **4.73**	**4.42** [38] (1050°C)
Ba	5400 to 7000 [7]				
Bi	2980 [22] 3225 [4] 3300 [3]	2835 [37] 3050 [8]		4.4 4.0	
C	2565 [36] 2615 [22]			(4.7)	3.93 [6]
Ca	3700 [4] 4000 [22] 7000 [7]	4475 [40]		(2.7)	2.24 [20]
Cd	3050 [7] 3130 [22] 3140 [4] 3302 [39]			(4.0)	
Co		3165 [40]	2900 [55] (Hexa-gonal) 3000 [55] (f-c cubic)	4.25 4.12	
Cs	7500 [5]	7400 [16]	6600 [50]	1.9	1.81 [39]
Cu	2665 [22] 3000 [3] 3033 [5]	2750 [8] 2955 [40] 3000 [11]		4.1 to 4.5	**4.38** [38]
Fe	2870 [22] 2944 [35]	3000 [11] 3155 [40]	**2620** [41]	**4.72**	
Ge		2880 [40]		(4.3)	
Hg	2600 [7] 3000 [12] 3040 [27]		**2735** [28]	**4.53**	
K	> 4360 [7] 6700 [3]	5500 [10] 5800 [47,7] 5800 [16] 6200 [21] 6500 [24] 7000 [25] 7000 [23]	5500 [50]	1.76 to 2.25	
Li	5260 [7]	4300 [10] 5200 [7] 5600 [16] 5800 [9]	5400 [50]	2.1 to 2.9	
Mg	3300 [4] 3820 [3] 7000 [7]	> 3650 [11]		(< 3.4)	
Mo	2854 [35]	3800 [46]		3.22 [46]	3.48 [46] **4.41** [32,36]

TABLE 3-2.—PHOTOELECTRIC AND THERMIONIC WORK FUNCTIONS OF THE METALS.—(*Continued*)

Metal	Threshold wave-length (A.u.)			ϕ Photoelectric, volts	ϕ Thermionic, volts
	I	II	III		
	No outgassing	Partial outgassing	Extended outgassing		
Na	5830 [3] 6100 [1]	5500 [7] 5500 [10] 6400 [16]	5000 [50]	1.90 to 2.46	
Ni	3050 [22] 3365 [39]	2700 [8] 3040 [40]	**2463** [56]	**5.01**	
Pb	2980 [22] 3110 [39] 3115 [4] 3550 [7]			(3.5 to 4.1)	
Pd		2800 [8]	**2488** [52]	**4.96**	4.99 [52]
Pt	2780 [22] 2800 [7] 2810 [35] 2840 [14] 3018 [39]	< 2100 [31] 2250 [34] 2540 [30] 2570 [17] 2675 [18] 2850 [14]	**1962** [42]	**6.30** [42]	**6.27** [42]
Rb		6800 [16] 6000 [7]	5700 [50]	1.8 to 2.2	
Rh			**2500** [48] (20°C) **2700** [48] (240°C)	**4.57**	**4.58** [48]
Se	2200 [4] 2670 [22]				
Sn	3075 [4] 3185 [22] 3411 [39] 3500 [7] 3620 [3]	3000 [11]	β—**2740** [43] γ—**2820** [43] liq.—**2925** [43]	**4.50** **4.38** **4.21**	
Sr	6000 [26]				
Ta	3148 [35]		**3050** [55] (20°C) **3150** [55] (700°C)	**4.05** **3.92**	**4.07** [32]
Th	3460 [22] 3700 [7]			(3.3 to 3.6)	**3.35** [36]
W	2615 [22] 2735 [35]	2300 [13] 2700 [34]	2650 [44] 2570 [44]	4.58	**4.52** [32]
Zn	3016 [4] 3200 [11] 3425 [22] 3760 [4] 4009 [39]	3182 [40]	3720 [51] 3460 [51] (Single crystal)	3.32 3.57	

The methods of measurement used by various authors are denoted as follows: (*S*) stopping potential, (*D*) spectral distribution curves, (*C*) complete photoelectric emission, (*F*) light filters, (*T*) thermionic measurements.

[1] F. K. RICHTMYER, *Phys. Rev.*, **30**, 385 (1910) (*D*).
[2] A. GOLDMANN and S. KALANDYK, *Ann. d. Phys.*, **36**, 589 (1911) (*D*).
[3] O. W. RICHARDSON and K. T. COMPTON, *Phil. Mag.*, **24**, 576 (1912) (*S*).
[4] A. L. HUGHES, *Phil. Trans. Roy. Soc.*, **212**, 205 (1912) (*S*).
[5] D. W. CORNELIUS, *Phys. Rev.*, **1**, 16 (1913) (*D*).
[6] I. LANGMUIR, *Phys. Rev.*, **2**, 450 (1913) (*T*).
[7] R. POHL and P. PRINGSHEIM, *Verh. d. Deutsch. Phys. Ges.*, **16**, 336 (1914); **15**, 111 (1913); **14**, 546 (1912) (*D*).
[8] S. WERNER, *Dissertation, Upsala* (1914) (*D*).
[9] R. A. MILLIKAN, *Phys. Rev.*, **7**, 380 (1916) (*S*).
[10] W. SOUDER, *Phys. Rev.*, **8**, 310 (1916) (*S*).
[11] A. E. HENNINGS and W. H. KADESCH, *Phys. Rev.*, **8**, 209 (1916) (*D*).
[12] J. B. DERIEUX, *Phys. Rev.*, **11**, 283 (1918) (*D*).
[13] C. F. HAGENOW, *Phys. Rev.*, **13**, 415 (1919) (*D*).
[14] O. STUHLMANN, *Phys. Rev.*, **15**, 549 (1920) (*D*).

3-22. Summary of the Effects of Gases on Photoelectric Thresholds. A concise summary of the various effects of gases for the purpose of formulating general rules and theories is not easy, since the effects themselves are very complicated and the experimental results are incomplete and often conflicting. The inadequacy of our experimental knowledge is evident when it is pointed out that practically nothing is known of the effects of gases on *clean* surfaces. The actual experimental tests usually involve either (1) a study of the changes in photoelectric properties produced by eliminating unknown gases from the surface by heating or other treatment, or (2) introducing a foreign gas into the presence of a surface which has itself been only partially denuded of gases occluded in it. There is ample evidence[1] that the photoelectric properties are determined by the amount of gas actually dissolved *in* the surface rather than on the pressure of gas in the tube. In Case 1, above, this would be an unknown and very complicated function of the previous history of the metal; in Case 2 it would depend on the nature and amount of the gas added and on the ability of the surface to absorb it, as well as upon the condition of the metal. It is not surprising, then, that apparently inconsistent results are often obtained, and that even the well-established results are often difficult to interpret.

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[15] M. J. Kelly, *Phys. Rev.*, **16**, 260 (1920) (*D*).
[16] E. F. Seiler, *Astrophys. Jour.*, **50**, 129 (1920) (*D*).
[17] O. Koppius, *Phys. Rev.*, **18**, 443 (1921) (*D*).
[18] R. Suhrmann, *Zeits. f. Phys.*, **13**, 17 (1923) (*D*, *T*).
[19] A. F. A. Young, *Proc. Roy. Soc.*, **104**, 611 (1923) (*D*).
[20] S. Dushman, *Phys. Rev.*, **21**, 623 (1923) (*T*).
[21] H. E. Ives and A. L. Johnsrud, *Astrophys. Jour.*, **60**, 231 (1924) (*D*).
[22] R. Hamer, *Jour. Opt. Soc. Amer.*, **9**, 251 (1924) (*D*).
[23] H. E. Ives, *Jour. Opt. Soc. Amer.*, **8**, 551 (1924) (*D*).
[24] J. W. Hornbeck, *Phys. Rev.*, **24**, 631 (1924) (*D*).
[25] O. W. Richardson and A. F. A. Young, *Proc. Roy. Soc.*, **107**, 377 (1925) (*D*).
[26] R. Döpel, *Zeits. f. Phys.*, **33**, 237 (1925) (*D*).
[27] S. Taubes, *Ann. d. Phys.*, **76**, 629 (1925) (*D*).
[28] C. B. Kazda, *Phys. Rev.*, **26**, 643 (1925) (*D*).
[29] R. Suhrmann, *Zeits. f. Phys.*, **33**, 63 (1925) (*C*).
[30] Chien Cha, *Phil. Mag.*, **49**, 262 (1925) (*D*).
[31] A. Woodruff, *Phys. Rev.*, **26**, 655 (1925); F. G. Tucker, *Phys. Rev.*, **22**, 574 (1923).
[32] S. Dushman, Rowe, Ewald, and Kidner, *Phys. Rev.*, **25**, 338 (1925) (*T*).
[33] K. H. Kingdon, *Phys. Rev.*, **25**, 892 (1925) (*T*).
[34] T. H. Harrison, *Proc. Phys. Soc. Lond.*, **38**, 214 (1926) (*D*).
[35] S. C. Roy, *Proc. Roy. Soc.*, **112**, 599 (1926) (*C*).
[36] C. Zwikker, *Proc. Amst. Acad. Sci.*, **24**, 1 (1926) (*T*).
[37] T. J. Parmeley, *Phys. Rev.*, **30**, 656 (1927) (*D*).
[38] A. Goetz, *Zeits. f. Phys.*, **43**, 531 (1927) (*T*).
[39] P. Lukirsky and S. Prilezaev, *Zeits. f. Phys.*, **49**, 237 (1928) (*S*).
[40] G. B. Welch, *Phys. Rev.*, **32**, 657 (1928) (*D*).
[41] A. B. Cardwell, *Proc. Nat. Acad. Sci.*, **14**, 439 (1928) (*F*).
[42] L. A. DuBridge, *Phys. Rev.*, **31**, 236 (1928); **32**, 961 (1928) (*D*, *T*).
[43] A. Goetz, *Phys. Rev.*, **33**, 373 (1929) (*D*).
[44] A. H. Warner, *Proc. Nat. Acad. Sci.*, **13**, 56 (1927); *Phys. Rev.*, **37**, 233 (1931) (*D*, *T*).
[45] A. Smits and H. Gerding, *Phys. Zeits.*, **30**, 322 (1929) (*D*).
[46] M. J. Martin, *Phys. Rev.*, **33**, 991 (1929) (*F*, *T*).
[47] R. Suhrmann, *Zeits. f. Phys.*, **52**, 453 (1928) (*D*).
[48] E. H. Dixon, *Phys. Rev.*, **37**, 60 (1931) (*F*, *T*).
[49] Computed by S. Dushman (*Rev. Mod. Phys.*, **2**, 383 [1930]) from measurements of K. H. Kingdon (*T*).
[50] Limiting value for thin film spontaneously deposited on metal plate in vacuum; A. R. Olpin, private communication (1931).
[51] C. E. Mendenhall and J. H. Dillon, private communication (1931). J. H. Dillon, *Phys. Rev.*, **38**, 408 (1931).
[52] L. A. DuBridge and W. W. Roehr, unpublished.
[53] R. P. Winch, *Phys. Rev.*, **37**, 1269 (1931).
[54] L. W. Morris, *Phys. Rev.*, **37**, 1263 (1931).
[55] A. B. Cardwell, *Phys. Rev.*, **33**, 2041 (1931).
[56] G. N. Glasoe, *Phys. Rev.*, **38**, 1490 (1931).

[1] O. Rietschel, *Ann. d. Phys.*, **80**, 71 (1926).

A summary of the experimental results on the effects of gases on photoelectric emission is given in Table 3-3. The first column shows the effect on the "total photoelectric sensitivity" of eliminating the gases

TABLE 3-3.—EFFECTS OF GASES ON THE PHOTOELECTRIC EMISSION OF THE METALS

Metal	Effect of outgassing	Gases which cause the sensitivity to		
		1	2	3
		Increase	Decrease	No change
Ag	(+) [1,2] (+) → (−) [44]	H_2 [2] H^+ [39]	O_2, CN Methane N_2 [2]	H_2, O_2
Al	(+) → (−) [3] (−) [15]			
Au	(+) → (−) [1,2,45]	H^+ [39]	Air [2]	
Bi			Air [4]	
C		NH_3, H_2, CO_2, air [38]		
Cd	(0) [42]			
Cu				
Fe	(+) → (−) → (+) [5]	O_2, H_2 [6]		
Hg		Wax vapor [7] H_2O vapor	H_2O vapor [7] (trace)	H_2 He, A, N [7]
K	(−) [8] (0) [9,10,42]	H_2 [11,12,35,40] O_2 [9] H^+ [13] O_2, H_2O, S, *et al.* [14] NO [41]	O_2	A, N [11] H_2 [13]
Li				
Mg	(−) [15]			
Mo	(−) [14] (+) [17]	H_2O [16]		
Na		O_2, S, P_2O, etc. [14]		
Ni	(−) [16] (+) → (−) [2]	H_2O [16]	Air, O_2 [2]	
Pb				
Pd	(+) → (−) [3,18,21,2,43] (−) [16]	H_2 [6,20,43] O_2 [6]	O_2 [2]	
Pd-Ag alloy		H_2 [19]		
Pt	(+) → (−) [22,23,3,18,1,25] (−) [26,27,28,24]	H_2 [1,2,22,23,24,25,26,34,37] NH_3 [29] O_2 [6] Wax and oil vapors [26,30] H^+ [39]	O_2 [25,26,2,30,31]	
Rh			H_2, O_2 [32]	
Ta	(+) [24,47] (−) [16] (0) [1]	H_2O [16]		
W	(−) [16] (+) [33]	H_2O [16]	O_2 [33] (λ_0 unchanged)	
Zn	(+) → (−) [36] (+) [46]			

T indicates that threshold measurements were made.

[1] R. SUHRMANN, *Zeits. f. Phys.*, **33**, 63 (1925); **19**, 1 (1923); **13**, 17 (1923) (*T*).
[2] L. A. WELO, *Phys. Rev.*, **12**, 257 (1918).
[3] J. KLUGE, *Ann. d. Phys.*, **82**, 432 (1927).

from a fresh specimen of the metal. The symbol (+) indicates an increase, (−) a decrease, (0) no change. In the last three columns are listed the gases which, when introduced into the cell, cause, respectively, an increase, a decrease, or no change in the total photoelectric sensitivity. In most cases an increased emission indicates a threshold shift to the red, and *vice versa*, but there are probably important exceptions. The few papers cited in the footnotes in which the thresholds themselves have been studied are indicated by a (*T*).

3-23. Discussion of Gas Effects.—An examination of Table 3-3 shows that in the case of hydrogen and oxygen, at least, it is perhaps possible to suggest tentative rules as to their effects on various surfaces. It will be noted that the effect of hydrogen is either zero or positive for nearly all cases. That is, when the gas has any effect at all it is to increase the photoelectric emission (decrease the work function). The effects of oxygen, on the other hand, are either zero or negative, that is, to decrease the emission. Furthermore, the metals on which hydrogen has the greatest positive effect are those which are known to have a particular affinity for it—the best examples being palladium and platinum which absorb this gas in large quantities. Similarly, the metals most profoundly affected by oxygen are those which readily absorb it or combine

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[4] T. J. Parmley, *Phys. Rev.*, **30**, 656 (1927).
[5] A. B. Cardwell, *Proc. Nat. Acad. Sci.*, **14**, 439 (1928) (*T*).
[6] H. Eichler, *Zeits. f. Wiss. Photog.*, **16**, 10 (1916); M. Ernst, *ibid.*, **17**, 35 (1918).
[7] H. K. Dunn, *Phys. Rev.*, **29**, 693 (1927); W. B. Hales, *Phys. Rev.*, **32**, 950 (1928) (*T*).
[8] G. Wiedmann and W. Hallwachs, *Verh. d. Deutsch. Phys. Ges.*, **16**, 107 (1914).
[9] R. Pohl and P. Pringsheim, *Verh. d. Deutsch. Phys. Ges.*, **15**, 625 (1913).
[10] H. E. Ives, S. Dushman, and E. Karrer, *Astrophys. Jour.*, **43**, 9 (1916).
[11] G. Wiedmann, *Verh. d. Deutsch. Phys. Ges.*, **18**, 333 (1916).
[12] O. W. Richardson and A. F. A. Young, *Proc. Roy. Soc.*, **107**, 387 (1925) (*T*).
[13] R. Suhrmann, *Phys. Zeits.*, **29**, 811 (1928); R. Suhrmann and H. Theissing, *Zeits. f. Phys.*, **52**, 453 (1928).
[14] A. R. Olpin, *Phys. Rev.*, **36**, 251 (1930) (*T*).
[15] K. Herrmann, *Verh. d. Deutsch. Phys. Ges.*, **14**, 563 (1912).
[16] H. Klumb, *Zeits. f. Phys.*, **47**, 652 (1928).
[17] M. J. Martin, *Phys. Rev.*, **33**, 991 (1929).
[18] W. Bennewitz, *Ann. d. Phys.*, **83**, 913 (1927).
[19] F. Krüger and A. Ehmer, *Zeits. f. Phys.*, **14**, 1 (1923).
[20] L. A. DuBridge, *Phys. Rev.*, **32**, 325 (1928) (*T*).
[21] L. A. DuBridge and W. W. Roehr, unpublished.
[22] O. Koppius, *Phys. Rev.*, **18**, 443 (1921).
[23] M. Sende and H. Simon, *Ann. d. Phys.*, **65**, 697 (1920).
[24] O. Rietschel, *Ann. d. Phys.*, **80**, 71 (1926).
[25] K. Herrmann, *Ann. d. Phys.*, **77**, 503 (1925).
[26] L. A. DuBridge, *Phys. Rev.*, **31**, 236 (1928); **29**, 451 (1927) (*T*).
[27] T. H. Harrison, *Proc. Phys. Soc. Lond.*, **38**, 214 (1926) (*T*).
[28] A. Woodruff, *Phys. Rev.*, **26**, 655 (1925) (*T*).
[29] H. Leupold, *Ann. d. Phys.*, **82**, 841 (1927) (*T*).
[30] L. Lockrow, *Phys. Rev.*, **19**, 97 (1922) (thermionic measurements).
[31] S. Werner, *Dissertation, Upsala* (1914) (*T*).
[32] E. H. Dixon, *Phys. Rev.*, **37**, 60 (1931) (*T*).
[33] A. H. Warner, *Proc. Nat. Acad. Sci.*, **13**, 56 (1927); *Phys. Rev.*, **33**, 815 (1929) (*T*).
[34] O. W. Richardson and Robertson, *Phil. Mag.*, **43**, 162 (1922) (contact potential measurements).
[35] R. Fleischer and H. Dember, *Zeits. f. Tech. Phys.*, **7**, 133 (1926); R. Fleischer, *Ann. d. Phys.*, **82**, 75 (1926).
[36] H. Küstner, *Ann. d. Phys.*, **48**, 893 (1915).
[37] E. Ladenburg, *Verh. d. Deutsch. Phys. Ges.*, **9**, 165 (1907).
[38] O. Stuhlmann and R. J. Piersol, *Nature*, **93**, 454 (1914).
[39] R. Suhrmann, *Zeits. f. Phys.*, **30**, 939 (1929).
[40] R. Fleischer and H. Teichmann, *Zeits. f. Phys.*, **61**, 227 (1930).
[41] R. Fleischer and H. Teichmann, *Zeits. f. Phys.*, **60**, 317 (1930).
[42] J. Elster and H. Geitel, *Phys. Zeits.*, **21**, 361 (1920).
[43] F. Stumpf, *Verh. d. Deutsch. Phys. Ges.*, **16**, 989 (1914).
[44] R. P. Winch, *Phys. Rev.*, **37**, 1269 (1931).
[45] L. W. Morris, *Phys. Rev.*, **37**, 1263 (1931).
[46] C. E. Mendenhall and J. H. Dillon, private communication (1931).
[47] A. B. Cardwell, private communication (1931).

with it—the outstanding example being tungsten. Metals which do not absorb either gas do not have their photoelectric properties affected by their presence. Thus the magnitude of the effect of a given gas on the photoelectric threshold of a metal is determined primarily by the tendency of the *metal* to absorb the gas.

The data in the table show also that the direction (positive or negative) of the effect of a gas on the photoelectric threshold is determined by the *nature of the gas* and is positive for hydrogen and negative for oxygen. It is possible that any electropositive gas would have the same effect as hydrogen while electronegative gases would behave like oxygen. It is seen that the inert gases have no effect. These facts suggest the formulation of the following tentative rule: *Electropositive gases cause an increase and electronegative gases a decrease in the photoelectric emission of surfaces which readily absorb them.* This rule, while purely qualitative, is in agreement with many, though not all, experiments. More data are needed to test its general validity.

It has been pointed out by Hallwachs and others that, in discussing the effects of gases, a distinction should be made between gases *ab*sorbed within the body of the metal and those *ad*sorbed on the surface. In the case of platinum, for example, it is suggested that *ad*sorbed gases retard the escape of electrons and that their presence causes the low sensitivity of a fresh specimen of this metal. The rapid removal of such gases during the first stages of heat treatment causes the observed initial rapid rise in sensitivity (see Fig. 3-8). On the other hand, the gases which have been *ab*sorbed within the body of the metal itself are assumed to assist in the ejection of electrons by decreasing the work function. They are eliminated from the metal only very gradually by the heat treatment, and their removal causes the slow decrease in sensitivity observed during prolonged heating. The Hallwachs theory thus puts the emphasis on the way the gas is held by the surface rather than the nature of the gas itself. It seems probable that both factors should be taken into consideration. If it should turn out that the gases most easily *ad*sorbed by platinum were the electronegative gases such as oxygen, while those *ab*sorbed were principally hydrogen, then the Hallwachs theory would be consistent with the rule proposed in the previous paragraph.

In the light of our present knowledge of the effect of gases on the photoelectric properties of metals, it is easy to see that many observers in the past have, on the basis of experiments which were themselves probably quite reliable, drawn conclusions which are certainly quite erroneous. This is due to the fact that the complexity of these phenomena has not always been realized. For example, much confusion has been caused by the failure to recognize that the effects of gases on photoelectric emission depend on the nature of the metal as well as on the nature of the gas present. If the elimination of occluded gases from one metal (*e.g.*, Pt) causes the photoelectric emission to decrease, it cannot therefore be concluded (as has often been done) that all gases *always* assist the photoelectric process in all metals. There

are some metals (*e.g.*, W, Ag) for which the photoelectric emission *increases* during outgassing. It is also conceivable that two samples of the same metal, prepared in different ways, might contain different kinds of gases—and their elimination might have different effects on the photoelectric properties.

Furthermore, in studying the effects of different gases, it has not always been recognized that extremely minute traces of certain gases (*e.g.*, a monomolecular layer) may have large effects on the photoelectric sensitivity. Thus if hydrogen is introduced into an experimental tube the effects observed might not be due to the presence of the hydrogen itself but to traces of oxygen or water vapor, or wax and oil vapors present in very small amounts as impurities, or released by the chemical action of the hydrogen. It is also possible that in many cases effects which have been attributed to the presence (or to the elimination) of gases may be due to alkali metals or other electropositive elements which may be present as impurities. As is pointed out in Sec. **3-25**, monatomic layers of these metals produce very large changes in the work function of surfaces on which they are formed, and in many cases they may be eliminated only by treatment at very high temperatures. Surface recrystallization of metals during heat treatment is another factor of great potential importance about which very little is known.

Finally, it must be pointed out that in spite of the large amount of data on the effects of gases but little is understood as to the real nature of their effects and of the mechanism by which they exert such a large influence on the surface work function. In view of recent developments in the Sommerfeld electron theory, to be discussed in Chapter VI, it can be said, however, that gases might affect the photoelectric properties of a surface either through a change in magnitude or shape of the surface potential barrier (W_a) or by a change in the potential (μ) of the electron gas within the metal. On this theory the photoelectric threshold of a surface is given by

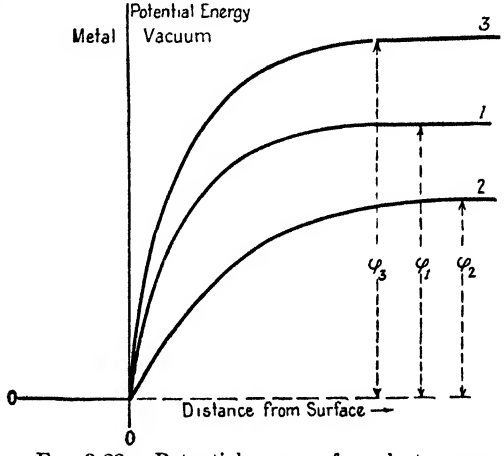

FIG. 3-23.—Potential energy of an electron near a metal surface. 1. Clean surface. 2. Surface with adsorbed layer of positive ions. 3. Surface with adsorbed layer of negative ions.

$$h\nu_0 = \phi e = W_a - \mu.$$

It is probable that the variation in potential energy of an electron in the vicinity of a clean metal surface is of the form shown by curve 1 in Fig. 3-23. It is easy to see that a layer of positive ions adsorbed on this surface would change this curve to the form shown in curve 2—thus lowering the work function. A layer of negative ions would give rise to curve 3, with a larger work function. Adsorbed layers of electropositive or electronegative materials may affect the surface in this way, and this would be consistent with the empirical rule suggested on page 80.

On the other hand, gases *ab*sorbed throughout the body of the metal may produce an expansion of the metal crystal lattice and this might result in a potential energy curve similar to curve 1 but with a smaller W_a.

A complication arises in the case of electronegative layers on the alkali metals, for Olpin and others have shown that such layers greatly increase the photoelectric

sensitivity. It appears that in this case a monatomic film of the alkali metal forms, by diffusion, on the *outside* of this electronegative layer, and this combination results in a greatly decreased work function.

The term μ (which is equal to the maximum kinetic energy of the electrons in the metal) would probably be unaffected by *ad*sorbed gas layers. Since μ depends on the number of free electrons per unit volume, however, it might well be altered by the presence of *ab*sorbed gases within the body of the metal.[1]

3-24. Effects of Gases on the Resistance of Metals.—Some light on the nature of gas effects on the photoelectric threshold may be fur-

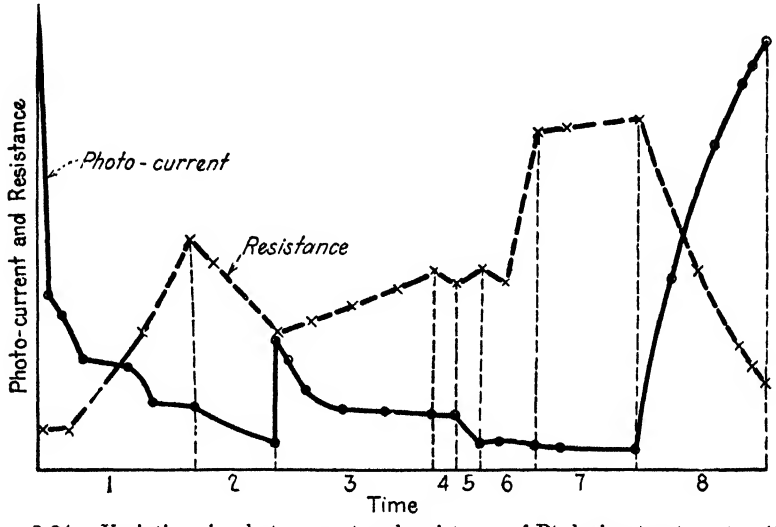

FIG. 3-24.—Variations in photocurrent and resistance of Pt during treatment. (*Herrmann.*) 1. Heated in vacuum. 2. Standing in vacuum. 3. Heated in vacuum. 4. Heated in O_2. 5. In vacuum. 6. In O_2. 7. In vacuum. 8. In H_2.

nished by studies of their relation to other electrical properties of the metal. The effects on the thermionic work function and on contact potential have already been noted, and some interesting effects on the optical constants of metal surfaces will be discussed in Sec. **5-10.**

The effects of gases on the *resistance* of metals have been studied by a number of observers and there has been an attempt to relate them to the photoelectric changes. Herrmann[2] and Janitzsky[3] have found that in the case of platinum and palladium the electrical *conductivity* and the photoelectric sensitivity always increase and decrease together during outgassing treatment, as shown in Fig. 3-24. Both are decreased on denuding the surface of gas, while introducing hydrogen causes both to

[1] Since this section was written, the following papers on matters related to it have appeared: "The Photoelectric Characteristics of Cadmium" by H. Bomke (*Ann. d. Phys.*, **10**, 257 [1931]), and "Photoelectric Properties of Thin Unbacked Gold Films" by R. P. Winch (*Phys. Rev.*, **38**, 321 [1931]).

[2] K. HERRMANN, *Ann. d. Phys.*, **77**, 503 (1925).

[3] A. JANITZKY, *Zeits. f. Phys.*, **31**, 277 (1925).

rise. The conclusion which has been drawn from this observation is that the presence of gases in some way lessens the average binding force between the atoms and the electrons, so that more electrons are nearly "free" and are more easily ejected by the incident light. An increase in the number of free electrons results also in an increase in conductivity.

However, Kleine,[1] and Puodziukynas[2] have found just the reverse effect, namely that the electrical resistance rather than the conductivity changed always in the same direction as the photoelectric effect. In fact, for Pt, Pd, and Fe, the resistance was found to be nearly a linear function of the amount of gas in the surface. The discrepancies between these two sets of experiments will possibly be found to be due to differences in experimental procedure in changing the gas content of the surfaces. It is not impossible that the effect is in one direction where minute quantities of gas are concerned, and in the opposite direction when large quantities of gas are introduced into the surface. Suhrmann,[3] in fact, has found that the resistance and also the emissivity of a platinum specimen first increase and then decrease as the gases are driven out. He explains his results by assuming three effects to be operating: (1) a decrease in the number of dissociated electrons due to the removal of H_2, causing an initial rise in resistance; (2) an expansion of the crystal lattice as gases absorbed in the metal are forced to the surface, causing a further slower rise in resistance; and (3) a contraction of the crystal after the gases have been removed, resulting in a slow decrease in resistance.

While the two phenomena are probably closely related, it is obviously impossible at present to draw any exact parallelism between the changes in resistance of a metal and in its photoelectric sensitivity. It might be argued that in any case a relation between the two would be purely accidental since the resistance is essentially a volume effect while the photoelectric sensitivity is primarily a surface phenomenon. Factors which might greatly affect the latter need have no appreciable effect on the former.

3-25. Effects of Other Surface Layers.—The photoelectric thresholds of the metals are greatly affected not only by surface layers of gas but also by layers of other materials, in particular the alkali metals, the alkaline earth and rare earth metals, and their oxides. The effects of alkali-metal layers have played a particularly important rôle in photoelectricity, but since most of the experiments have been carried on for the purpose of studying their effects on the selective photoelectric effect, a detailed discussion of them will be reserved for Chapter V. We shall mention here only the general effects of such layers on the surface work function.

[1] H. Kleine, *Zeits. f. Phys.*, **33**, 391 (1925).
[2] A. Puodziukynas, *Zeits. f. Phys.*, **46**, 253 (1928).
[3] R. Suhrmann, *Zeits. f. Phys.*, **19**, 1 (1923).

If a metal plate (*e.g.*, Pt) is mounted in a photoelectric cell into which a small quantity of an alkali metal has been introduced and if the plate is first thoroughly cleaned by heating and the cell then maintained at room temperature or below, it is found that there is a spontaneous increase in the photoelectric sensitivity of the plate owing to the deposition on it of a very thin (invisible) film of the alkali metal. The variation in the photoelectric threshold during this process has been studied by Ives and Olpin[1] for all the alkali metals. They find that, as the film builds up, the threshold shifts first toward longer and then, after a critical thickness has been passed, toward shorter wave-lengths, approaching finally the value characteristic of the alkali metal itself. There is evidence that this critical thickness corresponds to about a monatomic layer of the alkali metal. These effects may be ascribed to the fact that many of the alkali-metal atoms are adsorbed on the surface as positive ions, producing the alteration of the surface potential barrier shown in curve 2 of Fig. 3-23. (A similar effect may be caused by monatomic layers of electropositive gases.) The reduction of the work function reaches its maximum when the surface is just completely covered. Successive atomic layers may then be deposited without ionization and the surface thus becomes more like that of solid alkali metal and has a work function intermediate between that of the base metal and the monatomic layer.

If the alkali-metal film is deposited not on the surface of a clean metal but on one which already has an adsorbed layer of some electronegative material, such as oxygen, sulphur, or one of the great variety of materials studied by Olpin,[2] it is found that the maximum excursion of the threshold is much farther into the red. In many cases such surfaces may be sensitive to light of wave-lengths longer than 10,000A, and may show a sensitivity maximum in the vicinity of 7000A.[3] The importance of this discovery in the manufacture of commercial photoelectric cells will be recognized at once. The exact mechanism by which this great reduction of surface work function is accomplished is, however, not at all clear, though the problem is undoubtedly one which will receive a great deal of attention in coming years.

The *thermionic* properties of coated and composite surfaces of various types have been extensively studied and a thorough review of this field has recently been given by Dushman.[4] Thoriated-tungsten surfaces have received the most attention and the properties of such surfaces are of interest, not only because they probably have interesting photoelectric characteristics which have as yet been but little investigated, but because their behavior during activation or deactivation may be similar in many

[1] H. E. Ives and A. R. Olpin, *Phys. Rev.*, **34**, 117 (1929).
[2] A. R. Olpin, *Phys. Rev.*, **36**, 251 (1930).
[3] L. R. Koller, *Jour. Opt. Soc. Amer.*, **19**, 135 (1929).
[4] S. Dushman, *Rev. Mod. Phys.*, **2**, 381 (1930).

respects to that of metals from which gases or other impurities are being driven by heat treatment.

If a tungsten filament containing 1 or 2 per cent thoria (ThO_2) is heated for a short time in high vacuum at a temperature of 2700°K some of the thoria is reduced to metallic thorium which rapidly diffuses to the surface and evaporates. If the temperature is then lowered, the rate of evaporation is decreased, and at temperatures between 2000 and 2300°K an equilibrium condition is reached in which a certain fraction θ of the surface is covered by a monatomic layer of thorium. The fraction θ varies from zero for temperatures higher than 2300°, to approximately unity at temperatures near 2000°. If, after equilibrium has been reached at any temperature, the temperature of the filament is then lowered to below 2000°K the rates of diffusion and evaporation are so slow that θ does not change appreciably with time and the properties of the surface for any given value of θ may thus be studied. Langmuir[1] found that the work function of the surface varied linearly with θ from the value 4.52 volts for clean tungsten ($\theta = 0$) to 2.63 volts for a "fully activated surface" ($\theta = 1$).

Tungsten and oxidized tungsten covered with adsorbed caesium layers have been studied by Langmuir and Kingdon[2] and J. A. Becker.[3] If the tungsten filament is maintained in an atmosphere of caesium vapor, say at room temperature, then at low filament temperatures it is covered with a caesium layer and shows a thermionic work function of about 2.6 volts. At higher filament temperatures the caesium evaporates from the surface and the thermionic emission decreases with increasing temperature. If the caesium is deposited on oxidized tungsten the work function is reduced to 2 volts or less. Koller[4] has prepared surfaces of caesium on oxidized silver with a photoelectric threshold beyond 10,000A and with a thermionic work function of 0.65 volt for temperatures below about 200°C.

The oxide-coated filaments widely used in thermionic work because of their low work functions (1.0 to 2.0 volts) are prepared by coating a core metal (usually a Pt-Ni alloy) with a thick layer of a mixture of the oxides of Ca, Ba, and Sr. The phenomena observed with such filaments are much too complex to be discussed here, but it seems established[5] that the low work functions are probably due to an adsorbed layer of barium which forms during activation either at the surface of the core metal or on the outer surface of the oxide layer.

[1] I. Langmuir, *Phys. Rev.*, **22**, 357 (1923).

[2] I. Langmuir and K. H. Kingdon, *Phys. Rev.*, **24**, 510 (1924); I. Langmuir, *Indust. and Eng. Chem.*, **22**, 390 (1930).

[3] J. A. Becker, *Phys. Rev.*, **28**, 341 (1926).

[4] L. R. Koller, *Phys. Rev.*, **33**, 1082 (1929). See Sec. **5-11**.

[5] S. Dushman, *Rev. Mod. Phys.*, **2**, 444 (1930).

Only a beginning has been made in the photoelectric study of such surfaces. It has been found[1] that at high temperatures the thermionic emission from an oxide-coated filament is considerably increased when the filament is illuminated by light of wave-length less than 4000A, but this is probably not a pure photoelectric effect. Huxford[2] has recently found the threshold for a fully activated filament to be in the neighborhood of 9200A at room temperature. The *minimum* values of the work functions for certain composite surfaces are recorded in Table 3-4.

TABLE 3-4.—MINIMUM VALUES OF THE WORK FUNCTIONS FOR CERTAIN COMPOSITE SURFACES

Surface	Photoelectric		Thermionic, ϕ, volts
	λ_0, A.u.	ϕ, volts	
Li-W	6,700 [1]	1.83	
Na-Pt	5,900 [1]	2.08	
K-Pt	7,700 [1]	1.60	
Rb-Pt	7,950 [1]	1.56	
Cs-Pt	8,900 [1]	1.38	
Cs-W			1.36 [2]
Cs-O-W			0.714 [3]
Cs-CsO-Ag	>10,000 [4]	<1.23	0.65 [4]
Th-W	4,900 [5]	2.52	2.62 [6]
Th-Mo			2.58 [7]
Ba-Ag	7,900 [1]	1.56	
BaO-W			1.66 [8]
BaO-Pt	9,200 [9]	1.34	1.05 [10]

[1] H. E. IVES and A. R. OLPIN, *Phys. Rev.*, **34**, 117 (1929).
[2] J. A. BECKER, *Phys. Rev.*, **28**, 341 (1926).
[3] I. LANGMUIR and K. H. KINGDON, *Phys. Rev.*, **24**, 510 (1924).
[4] L. R. KOLLER, *Phys. Rev.*, **33**, 1082 (1929).
[5] L. B. LINFORD, *Phys. Rev.*, **36**, 1100 (1930).
[6] S. DUSHMAN and J. W. EWALD, *Phys. Rev.*, **29**, 857 (1927).
[7] S. DUSHMAN and N. B. REYNOLDS, quoted in *Rev. Mod. Phys.*, **2**, 403 (1930).
[8] J. M. EGLIN, *Phys. Rev.*, **31**, 1127 (1928).
[9] W. S. HUXFORD, *Phys. Rev.*, **37**, 102 (1931); **38**, 379 (1931).
[10] L. R. KOLLER, *Phys. Rev.*, **22**, 671 (1925).

In all of the above cases it is seen that the work function of the base-metal surface is greatly reduced by the presence of a monatomic layer of an electropositive material. Now, the effect on a work function of a layer of positive ions on a surface may be calculated from simple assumptions. Such a layer, together with its induced negative charge, constitutes a surface polarization and the change in potential of external points produced is given by the equation

$$\Delta\phi = 4\pi P = 4\pi Nea,$$

[1] *Cf.* K. NEWBURY and F. LEMERY, *Jour. Opt. Soc. Amer.*, **21**, 276 (1931). See Sec. 3-29.

[2] W. S. HUXFORD, *Phys. Rev.*, **37**, 102 (1931).

where N is the number of *ions* per square centimeter, e the electronic charge, and a the radius of the positive ion. According to J. A. Becker,[1] the work function of a tungsten surface covered with a monatomic layer of caesium, for example, is 1.36 volts. Hence $\Delta\phi = 4.52 - 1.36 = 3.16$ volts. Using for a the accepted value of 1.7×10^{-8} cm for caesium ions and solving for N we find,

$$N = 1.03 \times 10^{14} \text{ ions/cm}^2.$$

But the total number of *atoms* in a monatomic layer of caesium is $1/(1.7 \times 10^{-8})^2 = 3.5 \times 10^{14}$, which means that only about 29 per cent of the atoms are ionized. Similar calculations for barium and thorium give 14 and 6.8 per cent, respectively. On this basis it is therefore possible to obtain a simple and useful picture of the effects of adsorbed surface layers. Similar calculations could, of course, be made for the case of layers containing negative ions though there are not sufficient experimental data for such surfaces. Further light on this whole question is being obtained through studies of the variation of photoelectric and thermionic currents as a function of the accelerating field applied to draw them away from the surface.[2]

VARIATIONS OF THE PHOTOELECTRIC THRESHOLD

3-26. Effects of Temperature.—The dependence of the photoelectric effect on the temperature of the emitting surface has been the subject of many investigations. The problem is of great importance not only from the practical viewpoint of the user of photoelectric cells, but also because of its close relation to the theory of the photoelectric effect.

The first investigations in this field led to inconsistent results, due largely to the fact that they were carried out in air at atmospheric pressure and, therefore, subject to large secondary surface effects. It is now recognized that significant information on this question can be obtained only from experiments performed in a very high vacuum and on surfaces which have been thoroughly denuded of gases. The first experiments on the temperature effect at low pressures were reported by Lienhop,[3] who studied the photoelectric emission from carbon (soot) and platinum black at temperatures between room temperature and the temperature of liquid air. He determined the velocity distribution of the emitted electrons and found no observable change in these curves over this temperature range.

Almost simultaneously Millikan and Winchester[4] reported on an extensive series of measurements on 11 different metals, both the rate of discharge and the maximum velocity of emission being determined. In

[1] J. A. Becker, *Phys. Rev.*, **28**, 341 (1926); also a private communication (1931).

[2] See Sec. **3-31**, and also Sec. **6-15**.

[3] A. Lienhop, *Ann. d. Phys.*, **21**, 281 (1906).

[4] R. A. Millikan and G. Winchester, *Phil. Mag.*, **14**, 188 (1907).

the experimental arrangement, 11 disks of different metals were mounted on a single wheel in vacuum so they could be brought in succession into the path of the light and the photoelectric emission measured. The disks were polished, washed, and dried before being mounted in the tube and the pressure in the tube maintained at a value less than 10^{-5} mm Hg. The temperature was regulated by means of a furnace surrounding the tube, whose temperature could be held at any desired value between room temperature and 125°C. At higher temperatures electrostatic leaks made measurements unreliable. It was found that within this range the total photoelectric sensitivity to the light from a zinc spark remained constant within a range of accuracy varying from 0.2 to 1 per cent for the different metals. The maximum positive potential assumed by the plate under the action of the light was found also to remain constant[1] to within 0.03 volt. The metals studied were Cu, Ni, Ag, Zn, Mg, Pb, Sb, Al, and brass. The measurements on Al were extended up to a temperature of 340°C, the rate of discharge remaining constant within 2 per cent.

Measurements at higher temperatures were first made by Ladenburg[2] on Pt, Au, and Ir. He found that in the best vacuum then attainable, fresh surfaces of these metals did show a slight temperature effect, but that, after outgassing the surface by heating, this effect gradually disappeared and for a cleaned surface the photoelectric sensitivity remained practically constant up to 820°C, at which point the thermionic currents became large enough to be troublesome. The maximum velocity of emission was also measured by the magnetic deflection method and found to remain constant over the whole temperature range.

The alkali metals Na and K were studied by Dember[3] in 1907, who reported no effect of temperature on the photoelectric sensitivity between 20 and 100°C. Kunz[4] found no effect for Na-K alloy.

More recently a number of observers have made a careful study of the effect of temperature on photoelectric emission in extremely high vacua. The first of this series of experiments was reported by Nielsen,[5] who made his measurements on a solid block of aluminum which had been repeatedly heated in vacuum by high-frequency induction until all evolution of gas had ceased, the lowest pressures attainable by modern methods being maintained. Measurements of the photoelectric sensitivity to light from a quartz mercury arc were made as the specimen cooled from about 400°C down to room temperature, during which

[1] The constancy of the stopping potential, however, does not necessarily mean that there was no change in work function of the surface. Millikan's later results (see Sec. 2-5) showed that the stopping potential, for a given *receiving* electrode, is the same for all metals—and hence for different conditions of the same metal.

[2] E. Ladenburg, *Verh. d. Deutsch. Phys. Ges.*, **9**, 165 (1907).

[3] H. Dember, *Ann. d. Phys.*, **23**, 957 (1907).

[4] J. Kunz, *Phys. Rev.*, **29**, 174 (1909).

[5] J. R. Nielsen, *Phys. Rev.*, **25**, 37 (1925).

time the current was found to remain unchanged to within 0.5 per cent.

Koppius[1] and later DuBridge[2] studied the photoelectric effect from platinum specimens which had been heated many hours in vacuum and found no appreciable change in either the sensitivity or threshold up to 500°C. At higher temperatures an effect was observed which will be discussed later. Goetz[3] has found that the photoelectric threshold for either solid or liquid tin does not change with temperature as long as no crystal change or change of state occurs. Cardwell[4] reports a constant sensitivity for iron at temperatures below about 400°C. The photoelectric sensitivity and threshold of solid and liquid mercury have been studied under high-vacuum conditions by Miss Grützmann[5] and by Roller.[6] The former was unable to detect any change in the total photoelectric sensitivity of the thoroughly cleaned surface between 20 and −120°C, while Roller found no threshold change down to −190°C.

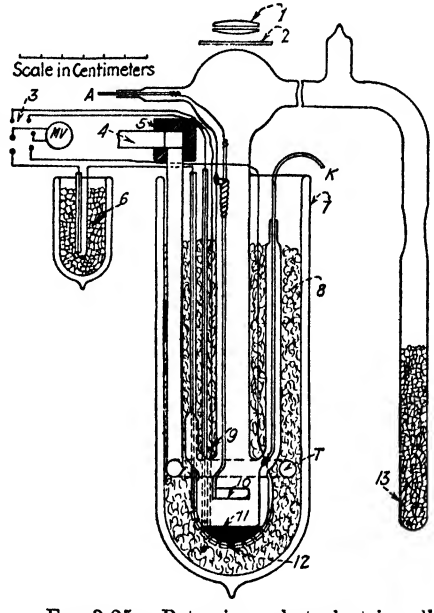

Fig. 3-25.—Potassium photoelectric cell for measurements at low temperatures. (*Ives and Johnsrud.*) 1. Lens. 2. Color filter. 3. Switch. 4. Tube for influx of cold air. 5. Rubber, serving as elbow for cold-air stream. 6. Ice in Dewar flask for one junction of thermocouple. 7. Dewar flask. 8. Glass wool. 9. One junction of differential thermocouple. 10. Nickel ring anode. 11. Pool of metal. 12. Junction of platinum-constantan thermocouple. 13. Charcoal tube.

The evidence of these experiments points to the conclusion that for temperatures up to 300°C the total photoelectric sensitivity, the maximum emission energy, and the photoelectric thresholds of most metals are not greatly affected by the temperature of the metal surface. In the best cases, changes in these quantities of the order of 1.0 per cent could have been detected. It was on the basis of this conclusion that it was at one time thought that the photoelectrons, ejected by light, must originate in the bound rather than the free electrons of the metal, since the latter were supposed to have a kinetic energy of thermal agitation equal to $\frac{3}{2}kT$. It was not realized, however, that most of the energy of the

[1] O. Koppius, *Phys. Rev.*, **18**, 443 (1921).
[2] L. A. DuBridge, *Phys. Rev.*, **29**, 451 (1927).
[3] A. Goetz, *Phys. Rev.*, **33**, 373 (1929).
[4] A. B. Cardwell, *Proc. Nat. Acad. Sci.*, **14**, 439 (1928).
[5] M. Grützmann, *Ann. d. Phys.*, **1**, 49 (1929).
[6] D. Roller, *Phys. Rev.*, **35**, 122 (1930).

ejected electrons came from the light and not from this thermal energy, and that the *total* energy of the photoelectrons (and therefore the photoelectric threshold) should change by only about 0.01 volt for a temperature change of 100°K. Most of the early experiments were not sufficiently precise to detect changes as small as this, and in more recent experiments changes as large as this have been actually detected. The most impor-

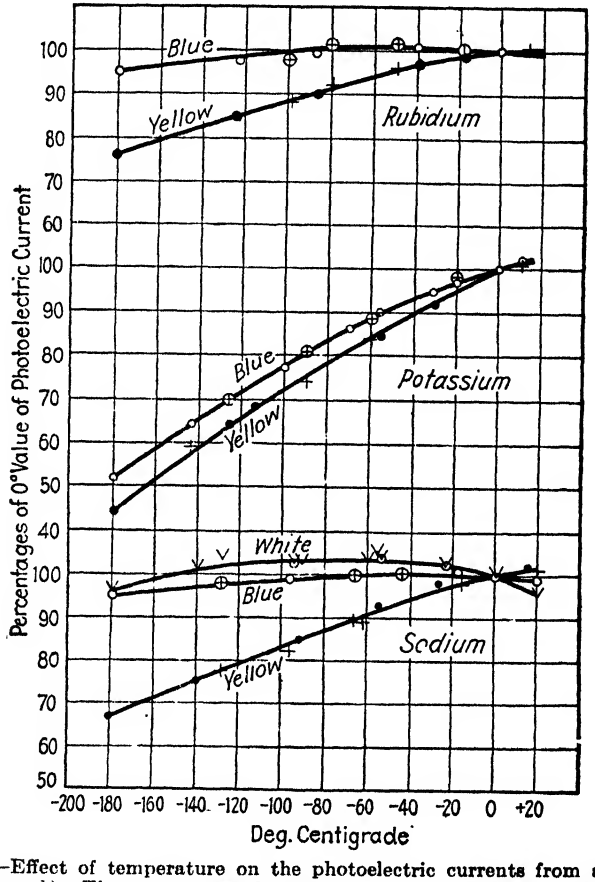

FIG. 3-26.—Effect of temperature on the photoelectric currents from alkali metals. (*Ives and Johnsrud.*) The two types of experimental points are for rising and falling temperature.

tant of these experiments deal with the alkali metals at low temperatures and the more refractory metals at quite high temperatures. These will be discussed more in detail.

3-27. Alkali Metals.—The variation with temperature of the photoelectric thresholds of the alkali metals was first investigated by Ives,[1] and a more complete study was later reported by Ives and Johnsrud.[2]

[1] H. E. IVES, *Jour. Opt. Soc. Amer.*, **8**, 551 (1924).

[2] H. E. IVES and A. L. JOHNSRUD, *Jour. Opt. Soc. Amer.*, **11**, 565 (1925).

The range of temperature covered was from −180 to 20°C. Sodium, rubidium, and potassium were studied in the form of condensed layers on glass and a further study was made of solid pools of potassium. One of the many different forms of photoelectric cell used is shown in Fig. 3-25.

In this cell, distilled potassium was collected in a pool at the bottom where it was carefully solidified so as to show a specular surface. The metal was illuminated by light passing through a color filter from above and the photocurrents collected by the nickel ring 10. The tube was placed in a Dewar flask and surrounded by glass wool,

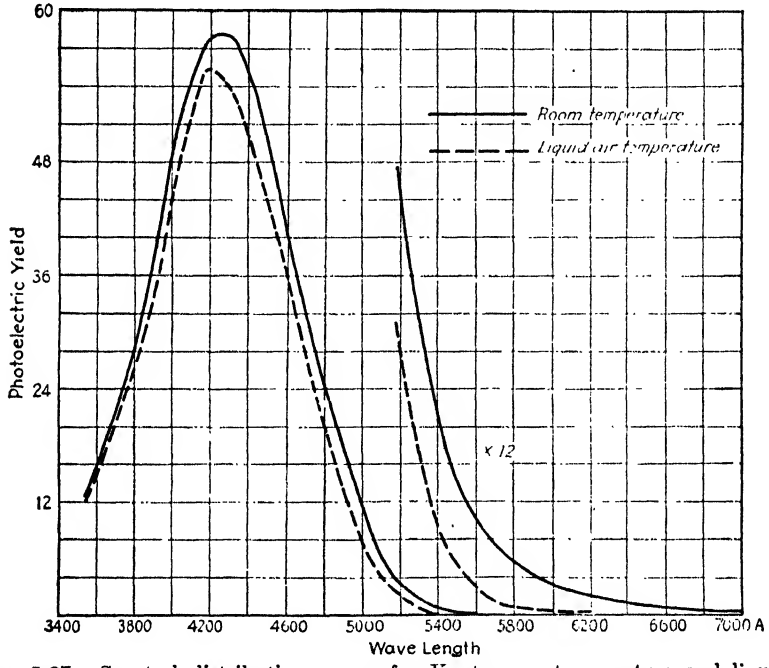

FIG. 3-27.—Spectral distribution curves for K at room temperature and liquid-air temperature. The curves to the right are magnified portions of the "feet," plotted to the same wave-length scale.

and was cooled by a blast of cold air from evaporating liquid air in another flask. The cold air was led in through the tube 4 and discharged against the walls of the cell through openings in the annular tube T. The temperature was measured by the platinum-constantan thermocouple 12, and was continuously variable from room temperature to the temperature of liquid air. In another form of tube used, the alkali metal was collected in a thin layer on a central cathode consisting of a hollow glass tube through which cold air could be circulated. An alkali-metal layer on the walls of the cell served as anode.

The temperature variation of the photocurrents excited in the alkali-metal films by light of various colors is shown in Fig. 3-26. The currents show a decided decrease in going from room temperature to the temperature of liquid air, the decrease being more pronounced for the longer wave-lengths. This suggests that there has been a shift of the threshold to

the violet at low temperatures. To obtain more accurate measurements of this shift the effect was studied for monochromatic light and the spectral distribution curves plotted. These are reproduced in Fig. 3-27. It will be noted that the curves do not plunge sharply into the wave-length axis, in spite of the precautions taken to eliminate scattered light—the usual cause for the "feet" of such curves. Nevertheless the intercept of the curve taken at liquid-air temperature is definitely on the short wave-length side of the curve for room temperature. The threshold shifted from about 7000A to 6200A, corresponding to an increase in the surface work function of 0.2 volt in this temperature range.

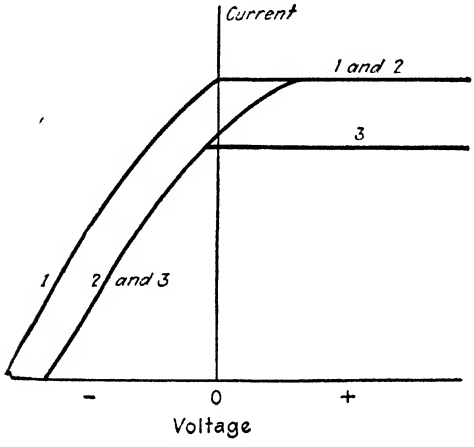

FIG. 3-28.—Idealized representation of voltage-current curves in alkali metal cells. 1. Cell at room temperature. 2. Anode cooled to liquid-air temperature. 3. Cathode and anode at liquid-air temperature.

The velocity distribution was also studied by observing the voltage-current curves (photocurrent *vs.* anode voltage) at the different temperatures. For this purpose another cell was employed in which both anode and cathode were made up of potassium layers on glass, the temperature of the two electrodes being independently variable. In Fig. 3-28, curve 1 is the voltage-current curve obtained with both anode and cathode at room temperature. Curve 2 is obtained when the *anode* is cooled to the temperature of liquid air. The change in stopping potential is due to a change in contact potential between the two surfaces. If now the *cathode* is cooled to liquid-air temperatures no further shift of stopping potential occurs, but there is a shift in the saturation point (curve 3). These are just the effects to be expected if cooling each surface, in turn, causes its work function to increase. The curves are, in fact, excellent examples of the relation between work function, stopping potential, and contact potential, first studied by Millikan and discussed in Sec. **2-5**. The change in the work function caused by a lowering of the temperature from 0 to −180°C again comes out to be about 0.2 volt.

A decrease in the photoelectric sensitivity of a potassium surface when cooled to liquid-air temperatures was also observed in 1925 by Hornbeck,[1] who found, however, by taking measurements at intermediate points, that the decrease was apparently not continuous but showed a decided "kink" in the curves at a temperature of −90°C. This was

[1] J. W. HORNBECK, *Phys. Rev.*, **24**, 631 (1924).

attributed to a crystal change at this point. In the investigation of Ives and Johnsrud, however, the photoelectric effect was carefully studied over a continuous range of temperatures from 20 to −180°C. No trace of a discontinuity was found, though this was carefully searched for.

The curves for sodium are of interest in the light of some results which had previously been reported by Burt,[1] who had found that, for sodium surfaces obtained by electrolysis of the metal directly through the soda glass walls of the tube, the photoelectric current excited by white light was the same at room temperature as at the temperature of liquid air. He therefore concluded that the photocurrent was independent of temperature and attributed Ives' results to the presence of impurities which could be removed by the procedure of electrolyzing the sodium into a highly

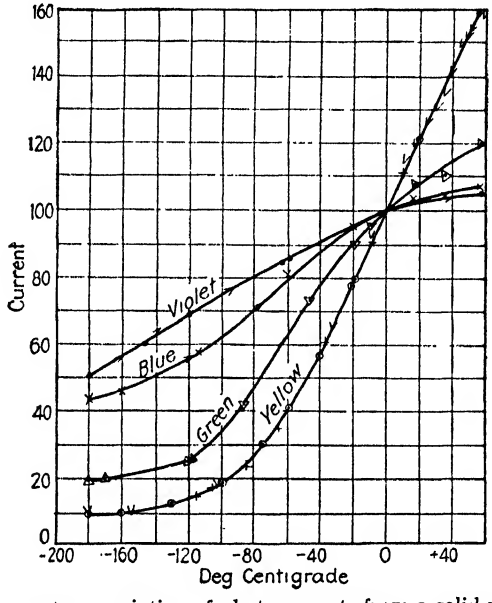

FIG. 3-29.—Temperature variation of photocurrents from a solid pool of potassium.

evacuated bulb. Figure 3-26 shows, however, that Ives' results are consistent with those of Burt, for the photoelectric effect with white light *is* practically the same at 20 and −180°C. Ives has shown, however, that at intermediate temperatures there is an *increase* in sensitivity missed by Burt. Furthermore, when red light is used instead of white the photocurrents decrease with decreasing temperature, showing an increase of the work function which is similar to that observed for K and Rb. It is unlikely that the carefully prepared surfaces employed by Ives and Johnsrud were appreciably affected by impurities.

Ives and Johnsrud found also that the decrease of the photocurrents with temperature for K was much exaggerated if, instead of using layers of the metal on glass as the sensitive surface, the specular surface of a solid, carefully annealed pool is employed (Fig. 3-29). In the latter case the sensitivity of the surface for yellow light, for example, is reduced to

[1] R. C. BURT, *Phil. Mag.*, **49**, 1158 (1925).

one-tenth of its value when the temperature is lowered from room temperature to that of liquid air. These authors, therefore, concluded that the whole temperature effect was due primarily to a change in surface structure caused by the cooling. If this be true, then the results of Ives and his co-workers would not be in disagreement with the empirical rule that, *the condition of the surface remaining unchanged*, the photoelectric effect is independent of the temperature of the illuminated surface. Ives' results emphasize the need for exercising great care in the interpretation of results on the temperature effect, a matter which is discussed more fully in Sec. **3-29.**[1]

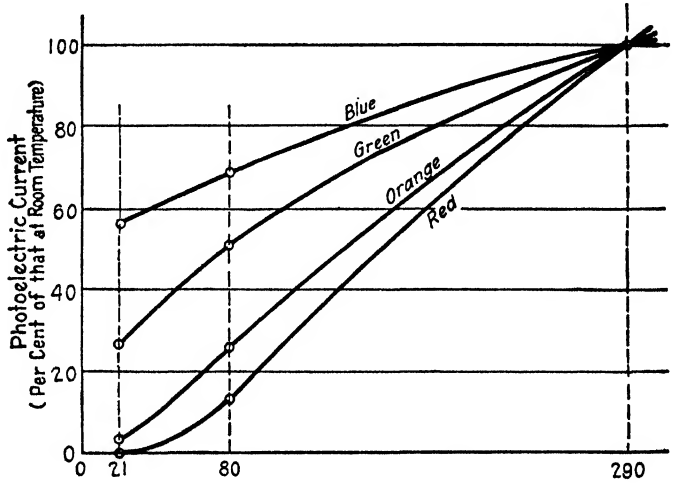

FIG. 3-30.—Variation of photocurrents from potassium between room temperature and the temperature of liquid hydrogen. (*McLennan, Matheson, and Niven.*)

Measurements on the photoelectric emission from potassium have been recently extended down to the temperatures of liquid hydrogen (21°K) by McLennan, Matheson, and Niven.[2] The curves obtained are reproduced in Fig. 3-30. It is found that the decrease in emission (increase in the work function) reported by Ives and Johnsrud continues without interruption down to the lowest temperature obtainable. The photoelectric current excited by red light practically disappears at the temperature of liquid hydrogen, while that for orange light is reduced to about 2 per cent of its value at room temperature. This indicates that there has been a shift in the threshold from the red into the orange part of the spectrum.

[1] These results on the alkali metals are in complete qualitative agreement with the recent theory of R. H. Fowler (*Phys. Rev.*, **38**, 45 [1931]) which attributes the temperature changes to changes in the thermal energy of the electrons. (See Sec. **6-30**).

[2] J. C. McLennan, Matheson, and Niven, *Trans. Roy. Soc. Can.*, **22**, 279 (1928).

3-28. The Photoelectric Effect at High Temperatures.—During recent years a number of studies have been made, principally by Mendenhall and his students, of the photoelectric effect at high temperatures for several different metals. All of the results show clearly that over sufficiently great temperature ranges the photoelectric threshold is not independent of the temperature.

In all of these investigations the metals under test were first thoroughly outgassed by heating for hundreds of hours in the highest attainable vacuum, and in each case what appeared to be the "limiting" value of the threshold for the clean metal had been reached. In some cases the temperature effects were complicated by changes in crystal structure, but these will be discussed separately in a following section.

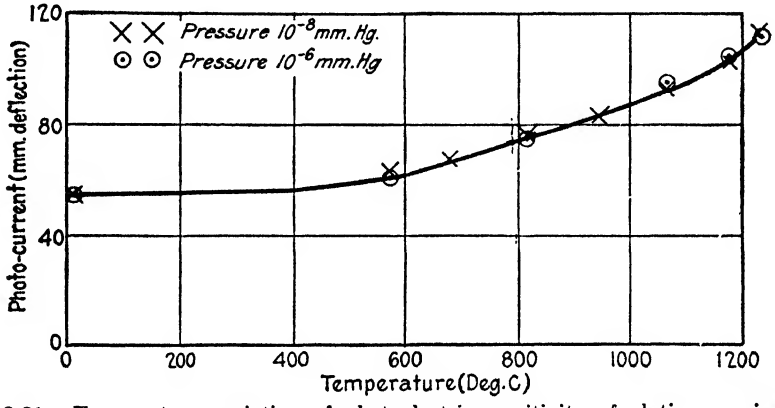

FIG. 3-31.—Temperature variation of photoelectric sensitivity of platinum, using full radiation of Hg arc.

The source of light used in each case was the mercury arc, supplemented by filters or by a monochromator.

A study of platinum was reported first by DuBridge,[1] who confirmed the result previously obtained by Koppius. that at temperatures above 500°C the photoelectric sensitivity of this metal to the total radiation of the mercury arc steadily increased, with a shift in the threshold to the red. The variation of the photoelectric sensitivity with temperature is shown in Fig. 3-31. It will be noted that between 500 and 1250°C there is a 100 per cent increase in the photoelectric current. Since the threshold for the specimen was at approximately 1962A the observed photocurrents represented the combined effect of only two mercury lines, 1943A and 1850A. Tests with filters showed that the increase in emission was accompanied by a shift of the threshold to the red, though the amount of the shift could not be accurately determined.

The photoelectric sensitivity of outgassed iron was studied as a function of temperature by Cardwell.[2] Using the total radiation of

[1] L. A. DuBridge, *Phys. Rev.*, **29**, 451 (1927).

[2] A. B. Cardwell, *Proc. Nat. Acad. Sci.*, **14**, 439 (1928).

the mercury arc, it was found that while the photocurrents were nearly constant up to about 400°C. they showed, at higher temperatures, a definite decrease. At about 750° complications due to crystal changes set in, and it is possible that the change between 400 and 750° is due to the beginning of this crystal change.

A decrease in the photoelectric sensitivity with increasing temperature up to 1000°C was also found for molybdenum by Martin,[1] whose results are shown in Fig. 3-32. However, since the value of the work function observed in these experiments is considerably less than the

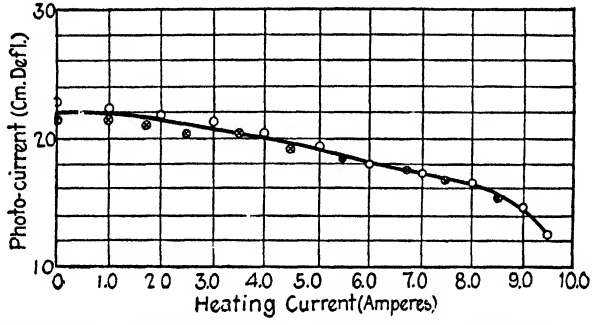

FIG. 3-32.—Temperature variation of the photoelectric sensitivity of molybdenum. (*Martin.*)

value for clean molybdenum reported by Dushman and his co-workers, it is possible that the temperature effect observed is due to the elimination of electropositive impurities from the surface.

The total photoelectric emission of thoroughly outgassed cobalt excited by light from a quartz mercury arc was found by Cardwell[2] to increase by about 50 per cent between room temperature and 700°C. There was no evidence of a crystal change in this region, though a sharp increase in photoelectric emission due to a change in crystal structure was observed at 850°C.

For outgassed rhodium Dixon[3] has recently reported a 130 per cent increase in photoelectric sensitivity to the mercury arc between room temperature and 950°C. Between 20 and 240°C the increase was somewhat irregular and appeared to be associated with a crystal change, but above about 240° there was a linear relation between photoelectric current and the heating current passing through the specimen (Fig. 3-33). Tests with filters showed that the threshold remained between the mercury lines 2652A and 2752A over this temperature range, so that if there was any shift it was less than 100A.

The above results show that for Pt, Co, and Rh there is a definite increase in the total photoelectric sensitivity with temperature which is

[1] M. J. MARTIN, *Phys. Rev.*, **33**, 991 (1929).
[2] A. B. CARDWELL, *Proc. Nat. Acad. Sci.*, **15**. 544 (1929).
[3] E. H. DIXON, *Phys. Rev.*, **37**, 60 (1931).

probably not due to secondary effects such as crystal changes, outgassing, etc. For Mo and Fe there is a decrease in sensitivity which *may* be due to secondary effects. Until recently, however, there had been no accurate measurements of the effects of temperature on the photoelectric *threshold* of clean metals, as determined by spectral distribution curves. In 1931 a series of studies of this type was made for the metals silver, gold, and tantalum. These results are of considerable interest and may be summarized as follows:[1]

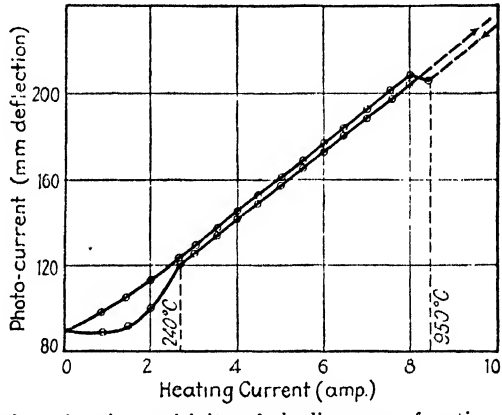

FIG. 3-33.—Total photoelectric sensitivity of rhodium as a function of heating current. (*Dixon.*)

For a gold specimen which had been subjected to an outgassing treatment for 1800 hr in high vacuum, the photoelectric threshold at room temperature was found by Morris[2] to be in the vicinity of 2560A. As the temperature is raised the threshold shifts to the red, reaching a value of 2610A at 740°C, the highest temperature used. (The spectral distribution curves are shown in Fig. 3-34.) This is a change in work function of approximately 0.09 volt for a temperature range of 720°, an average of 1.2×10^{-4} volt/deg.

If the photoelectric current excited by monochromatic light (*i.e.*, the "spectral sensitivity") is plotted as a function of the temperature of the specimen, the curves shown in Fig. 3-35 are obtained. It will be noted that for wave-lengths near the threshold there is a very rapid rise with temperature while for much shorter wave-lengths there is actually a decrease in sensitivity. This is also seen in the fact that the curves of Fig. 3-34 intersect at a wave-length approximately 200A from the threshold. This probably accounts for the fact that other observers have found the *total* photoelectric sensitivity of the metals to be nearly independent of temperature.

[1] The authors are indebted to Professor Mendenhall, who informed them of these results before their publication.

[2] L. W. MORRIS, *Phys. Rev.*, **37**, 1263 (1931).

Quite similar results were obtained by Winch[1] for thoroughly degassed silver, the curves for 20 and 600°C being shown in Fig. 3-36. There is a

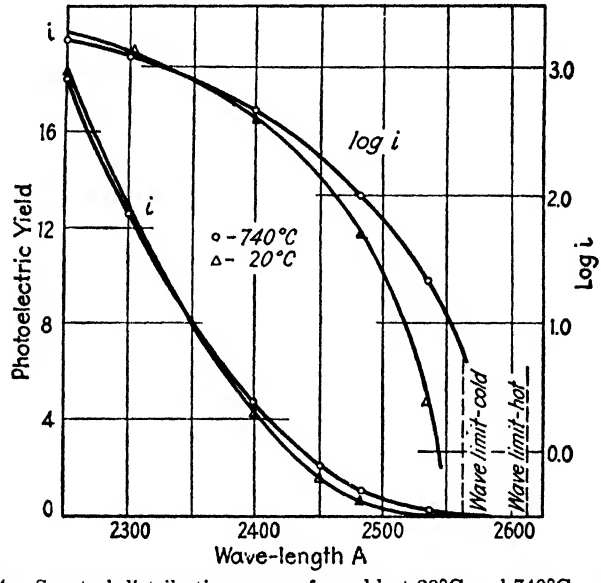

FIG. 3-34.—Spectral distribution curves for gold at 20°C and 740°C. (*Morris.*)

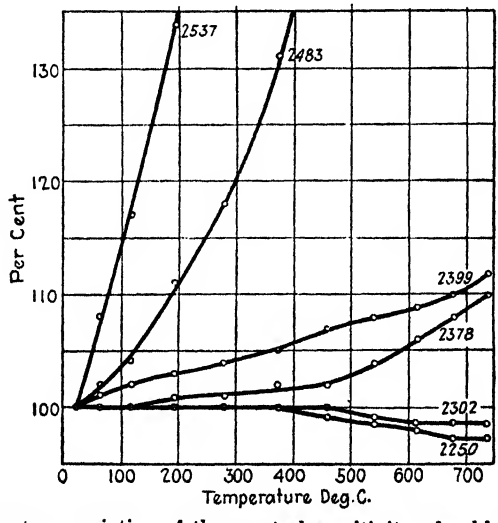

FIG. 3-35.—Temperature variation of the spectral sensitivity of gold for different wavelengths.

shift in the long-wave limit from 2610A to 2710A for this temperature range. This corresponds to an average temperature coefficient of the work function of approximately 3.0×10^{-4} volt/deg, or over twice

[1] R. P. WINCH, *Phys. Rev.*, **37**, 1269 (1931).

that observed for gold. Most of the shift, however, took place at temperatures above 200°C, as can be seen from the curves of Fig. 3-37,

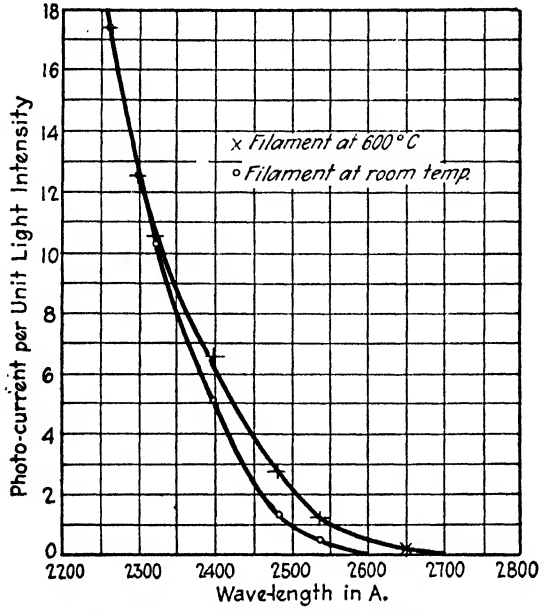

FIG. 3-36.—Spectral distribution curves for silver at 20°C and 600°C. (*Winch.*)

which show the changes in sensitivity for light of different wave-lengths. Special tests proved that these changes in spectral sensitivity were not

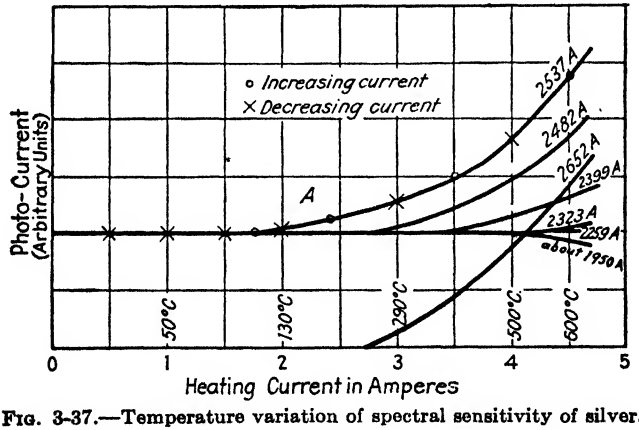

FIG. 3-37.—Temperature variation of spectral sensitivity of silver.

due to a change in the absorption coefficient of the surface for ultra-violet light, since this was found to remain constant.

Spectral distribution curves obtained by Cardwell[1] for tantalum are reproduced in Fig. 3-38. These have the same characteristics as the

[1] A. B. CARDWELL, unpublished.

curves for silver and gold, except that the intersection of the curves for high and low temperatures is considerably more marked. The intercepts show a shift in λ_0 of 100A for the temperature range 20 to 700°C, representing an average temperature coefficient of the work function of 1.85×10^{-4} volt/deg.

These results are surprising in that they show a shift of the threshold with temperature which is of the order of magnitude of that which

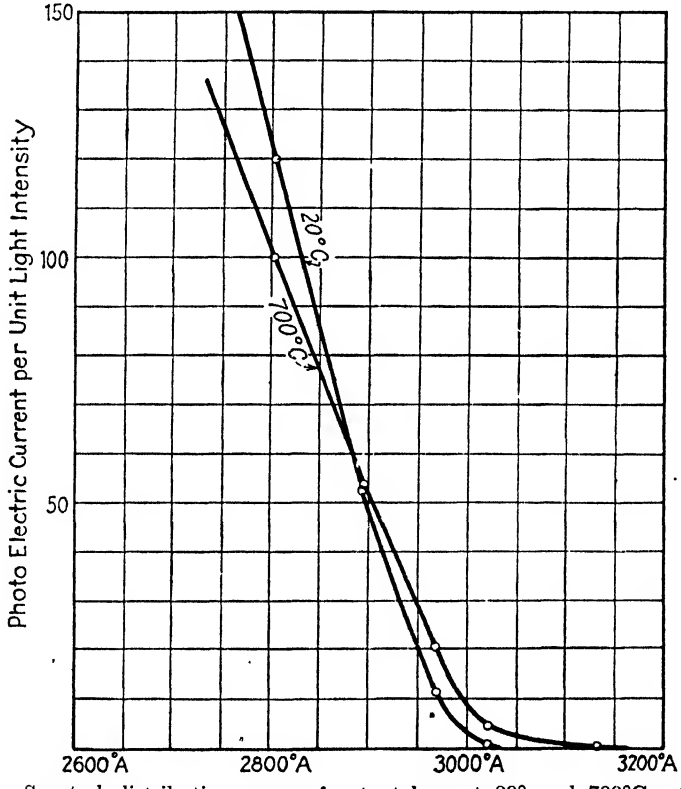

FIG. 3-38.—Spectral distribution curves for tantalum at 20° and 700°C. (*Cardwell.*)

would have been expected on the classical electron-gas theory of metals, *i.e.*, 10^{-4} volt/deg. It thus appears that the apparent conflict between this theory and the photoelectric results may have been founded on insufficient experimental data. Detailed calculations of the magnitude of the temperature coefficient of the threshold to be expected on the Sommerfeld electron theory have just recently been made by R. H. Fowler.[1] It appears that the "tailing off" of the curves at the higher temperatures can be quantitatively accounted for on this theory, and is due to the thermal energies of the electrons in the metal. In fact,

[1] See Sec. 6-30.

the curves for all temperatures above 0°K should show an asymptotic approach to the frequency axis, so that the value of the threshold obtained will depend greatly on the judgment of the observer and on the sensitivity of the current-measuring instrument. A "true" photoelectric threshold thus exists only at the absolute zero. Fowler has, however, devised a method for obtaining the value of this true threshold from spectral distribution curves taken at ordinary temperatures, and the values so obtained are in some cases as much as 120A farther to the violet than the "apparent" values obtained by extrapolation of spectral distribution curves taken at room temperature. Fowler's paper thus has introduced

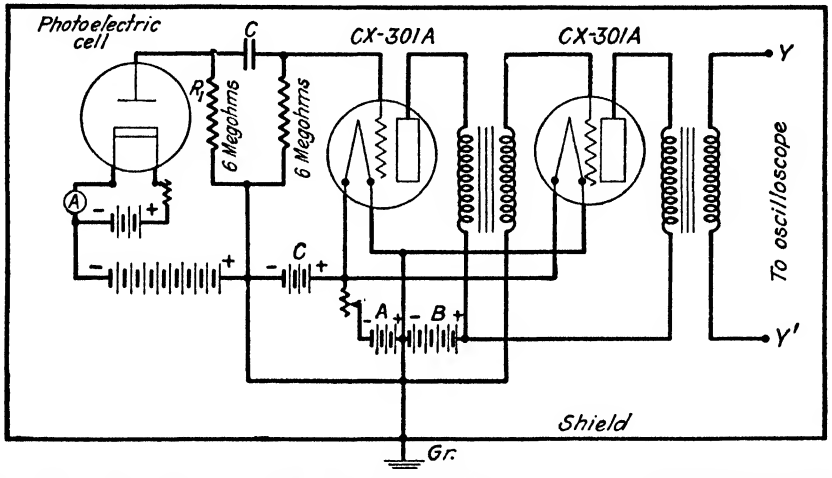

FIG. 3-39.—Circuit for amplifying rapidly varying photocurrents to separate them from steady thermionic currents. (*Ramadanoff.*)

a new viewpoint into the discussion of temperature effects, so that future experiments should be designed not to measure the "temperature dependence of λ_0," but to yield results which can be analyzed by Fowler's method to determine the true threshold. Fowler's theory is in excellent agreement with the results of Winch, Morris, and Cardwell, discussed above, but it is highly desirable that it should be further checked by accurate measurements on other metals and over a greater range of temperature.[1]

Measurements of the photoelectric current at high temperatures can, of course, be taken only with the higher melting point metals, and only such of these as can be obtained in the form of a wire or strip which can be conveniently heated to any desired temperature by means of an electric current. For temperatures below those at which thermionic currents become appreciable no special technique is required, except that precautions must be taken against electrostatic effects due to the heating of the glass walls of the tube. When thermionic currents are of the same order of

[1] This has recently been done by DuBridge and Roehr for clean Pd. The results (soon to be published) furnish further quantitative verification of Fowler's theory.

magnitude as the photoelectric currents they may be balanced out by means of a potentiometer, or one may take as the photocurrent the *change* in current observed when the light is admitted to the cell. Since it is difficult to keep the thermionic currents constant to better than 0.5 per cent it is usually not possible to obtain accurate measurements beyond the point where the thermionic currents are more than twenty times larger than the photocurrents.

Quite recently, however, Ramadanoff,[1] in studying the photocurrents from oxide-coated cathodes, has developed a technique of measurement which may allow the extension of photoelectric readings to much higher temperatures. His method was to illuminate the specimen by light passing through a rotating disk, the openings in the disk being of such a shape as to give a sinusoidal variation in the intensity of the beam. By means of a transformer-coupled amplifier (Fig. 3-39) the resulting current is amplified and made to operate a cathode-ray oscilloscope. The height of the wave appearing on the screen is taken as proportional to the photoelectric sensitivity of the illuminated surface. Obviously in this way any steady or slowly varying thermionic currents, or other "dark currents," are completely eliminated, since only the sinusoidal component of the total current is measured.

3-29. Temperature Effect in Composite Surfaces.—In the preceding sections attention has been confined to clean metal surfaces for which a direct effect of temperature on the photoelectric emission has been studied. It is well known that very much larger temperature effects are obtained for composite surfaces, due presumably to a change in the nature, and hence in the work function, of the surface. Thus, for surfaces which have not been freed of occluded gases, large and irregular changes of the photoelectric current with temperature are usually observed owing to changes in the surface gas layers. For metal surfaces exposed to alkali-metal vapors, Ives[2] has found that, as the temperature of the metal is increased, the photoelectric emission excited by visible light increases slowly at first, then rises suddenly to a very sharp peak, and finally falls to zero (see Fig. 5-14 page 156). In this case, heating the surface changes the thickness of the condensed alkali-metal film, and the photoelectric effect reaches its maximum for a certain critical thickness. At high temperatures the alkali metal is completely driven off and the clean platinum is insensitive to visible light. The thermionic currents reach a maximum at about the same temperature as the photocurrents, and are of the same order of magnitude.

For platinum filaments coated with barium and other alkaline-earth oxides Case[3] first reported a 1400-fold increase in the currents excited by light from a mercury arc as the temperature was raised from 20°C to a dull-red heat. Similar effects, though of smaller magnitude, have been reported by Crew, Koppius, Newbury, and others.[4] The largest photocurrents are obtained when the thermionic emission from the fila-

[1] D. Ramadanoff, *Phys. Rev.*, **37**, 884 (1931).

[2] H. E. Ives, *Astrophys. Jour.*, **64**, 128 (1926).

[3] T. W. Case, *Phys. Rev.*, **17**, 398 (1921).

[4] W. H. Crew, *Phys. Rev.*, **28**, 1265 (1926); O. Koppius, *Phys. Rev.*, **18**, 443 (1921); K. Newbury, *Phys. Rev.*, **34**, 1418 (1929); C. E. Berger, *Phys. Rev.*, **34**, 1566 (1929).

ment is also large, and it has been suggested that they are not true photoelectric currents but simply represent an increase in the thermionic current produced by the action of the light. Newbury and Lemery[1] have recently found that these extra currents excited by light reach a sharp maximum at a temperature near 1000°C and then fall off at higher temperatures. The maximum value was about 7 micro-amperes at 1000°C and at this temperature the light currents were about 2 per cent of the thermionic current.

A more extensive investigation of this problem has recently been reported by Ramadanoff,[2] using the experimental technique described in the previous section. With steady light from a mercury arc it was found that the photoelectric currents (difference between currents with light on and light off) increased by a factor of 100 between 500 and 750°C where a maximum was reached. But if interrupted light is used (1000 cycles/sec) the alternating component of the resulting current increases by a factor of only 16 over the same temperature range. It was assumed that only the latter represented the true photoelectric currents, since they followed without lag the variations in light intensity. The additional currents excited by *unvarying* light were assumed to be due to a sluggish action of the light such as might be produced by a change in space-charge conditions or (although this was not mentioned) a photochemical effect at the filament surface. The rapid increase (sixteen-fold) in the true photoelectric currents is ascribed to the change with temperature of the active layer of barium at the surface.

3-30. Variation of the Photoelectric Threshold with the Crystal Structure of the Surface.—During the past few years a number of studies have been made of the changes in the photoelectric properties of a surface when it is taken through the melting point or a point where a crystal transition takes place. Dember[3] had found in 1907 that there was no change in the photoelectric sensitivity of sodium and potassium in passing through the melting point, but no further experiments were reported on this subject until 1925. However, Goetz[4] and Seiliger[5] had found a change in the thermionic emission of samples of iron when passing through a crystal modification, so that an analogous change in the photoelectric properties would be expected. Farnsworth[6] and Davisson and Kunsman[7] had found marked changes in the electron-reflection curves depending on the surface crystallization, recently brought into prominence through

[1] K. Newbury and F. Lemery, *Jour. Opt. Soc. Amer.*, **21**, 276 (1931).
[2] D. Ramadanoff, *Phys. Rev.*, **37**, 884 (1931).
[3] H. Dember, *Ann. d. Phys.*, **23**, 957 (1907).
[4] A. Goetz, *Phys. Zeits.*, **24**, 377 (1923); **26**, 206 (1925).
[5] S. Seiliger, *Zeits. f. Phys.*, **38**, 443 (1926).
[6] H. E. Farnsworth, *Phys. Rev.*, **27**, 413 (1926).
[7] C. Davisson and C. Kunsman, *Phys. Rev.*, **22**, 242 (1923).

the remarkable electron-diffraction experiments of Davisson and Germer.[1] Dowling[2] also found some evidence for supposing that the contact potential between two metals was influenced by a surface crystallization of one of them. These experiments led Mendenhall[3] to suggest that possibly the effects of surface crystallization were playing a larger rôle in photoelectric and thermionic experiments than had been suspected. A direct test of the effect of surface crystallization on the photoelectric effect was first reported by Parmeley,[4] who examined the photoelectric emission from a single crystal of bismuth, comparing it with the effect of the ordinary polycrystalline material. No difference in photoelectric properties was detected. The experiments were not entirely satisfactory, however, since they were not performed under thoroughly gas-free conditions and as a result the photocurrents were found to change spontaneously with time. Linder[5] then performed the experiment of rotating a single crystal of bismuth, in the form of a rod, in front of a light source so that the various crystal faces were illuminated in succession. It was found that during the rotation of the rod there was a periodic change in the photoelectric current, an indication that the various crystal faces were not equally sensitive. The crystal was suspended in a well-evacuated tube but wax vapors were present and the crystal itself could not be thoroughly outgassed.

A more conclusive set of results was obtained by Cardwell,[6] who measured the photoelectric sensitivity to a mercury arc of a strip of iron as its temperature was raised through the points where the changes from α- to β- to γ-crystal forms take place. The α- and β-forms of iron both have a body-centered cubic structure but with different lattice constants, while the γ-form is a face-centered cubic. The iron was first given a thorough heat treatment and the pressure within the photoelectric tube reduced to less than 10^{-8} mm Hg, all wax vapors being eliminated. The variation of the photoelectric current with heating current through the strip is shown in Fig. 3-40, the points where the changes in crystal structure are known to take place being indicated. It is seen that there is a sudden change in slope of the curve at both crystal transformations in such a direction as to indicate that the β-form is somewhat more sensitive than either the α- or γ-crystal forms. It was not possible to tell whether the change was accompanied by a change in threshold. It was found, however, that there was an exactly analogous change in the thermionic emission at the transition temperatures.

[1] C. Davisson and L. H. Germer, *Phys. Rev.*, **30**, 705 (1927).
[2] P. H. Dowling, *Phys. Rev.*, **31**, 244 (1928).
[3] C. E. Mendenhall, *Jour. Franklin Inst.*, **201**, 269 (1926).
[4] T. J. Parmeley, *Phys. Rev.*, **30**, 656 (1927).
[5] E. G. Linder, *Phys. Rev.*, **30**, 649 (1927).
[6] A. B. Cardwell, *Proc. Nat. Acad. Sci.*, **15**, 544 (1929); **14**, 439 (1928).

A study of the photoelectric properties of cobalt as affected by changes in crystal structure has also been reported by Cardwell. The experiments

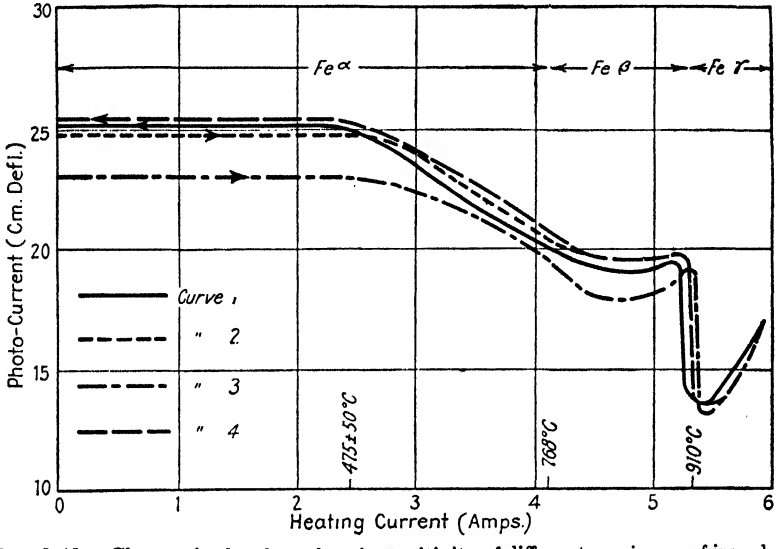

FIG. 3-40.—Changes in the photoelectric sensitivity of different specimens of iron during crystal transitions. The change from α- to β-iron occurs at 768°C and from β to γ at 910°C. (*Cardwell.*)

were carried out at pressures of less than 3×10^{-8} mm Hg and extended outgassing methods were employed. The source of light was the mercury

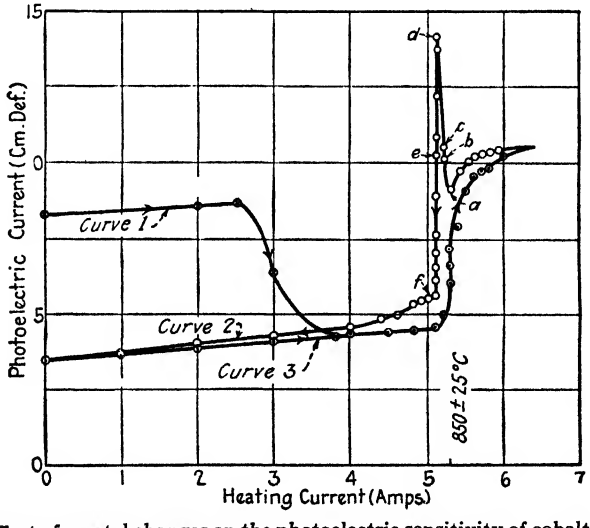

FIG. 3-41.—Effect of crystal changes on the photoelectric sensitivity of cobalt. (*Cardwell.*)

arc and only the total currents excited by the arc were studied. The variation in photocurrent with heating current through the specimen is

shown in Fig. 3-41. Starting with the specimen at room temperature, the photocurrent increases slowly with temperature up to 850°C, at which point a sudden increase to a much higher value is observed (curve 3). This increase is probably associated with the transition from the hexagonal close-packed to the face-centered cubic lattice. This transition is usually observed at somewhat lower temperatures, but it depends greatly on the purity of the sample, occurring at higher temperatures for pure samples. The cobalt used in this investigation was extremely pure and the extended heat treatment and outgassing possibly tended to raise the transition temperature. The usual "resistance-hysteresis" characteristic of the crystal change occurred at the same temperature as the photoelectric discontinuity.

On cooling the specimen back through 850°C, a striking phenomenon is observed (curve 2). The photoelectric sensitivity rises to a very sharp maximum just at the transition temperature, and then falls to the value characteristic of the lower temperatures. Thus it appears that during the crystal change a surface of very high sensitivity is developed, but is stable only through a very limited temperature range. No explanation for this phenomenon has been offered.

When the specimen is cooled quickly from a temperature above 850° to room temperature and then heated slowly, the behavior indicated by curve 1 is obtained. The high sensitivity at room temperature is attributed to a supercooling effect, and an X-ray analysis showed that the rapidly cooled specimen was characterized by the cubic, and the slowly cooled by the hexagonal lattice.

It was found that the changes in the thermionic currents were exactly analogous to those in the photocurrents, although the thermionic currents at these temperatures were many times smaller than the photoelectric. A study of the surface work functions for the various crystal forms of cobalt would be of great interest.[1]

The effects of crystal changes and changes in state on the photoelectric threshold of tin were studied with great thoroughness by Goetz[2] in 1929. Tin was chosen as the metal most susceptible to study in this respect since it shows a crystal transition and a change from solid to liquid in an easily available temperature range and has a sufficiently low vapor pressure to make accurate measurements on the liquid surface feasible. A diagram of the rather elaborate apparatus employed is shown in Fig. 3-42. Pure tin, which has been preheated in an atmosphere of hydrogen to reduce all oxides, is introduced through a capillary tube R_2 into a pyrex cup V in a highly evacuated cell which can be heated by an electric furnace H. The tin was further heated to high temperatures

[1] Dr. Cardwell has informed the authors that he has found photoelectric thresholds of about 3000A and 2900A for the cubic and hexagonal forms, respectively.

[2] A. Goetz, *Phys. Rev.*, **33**, 373 (1929).

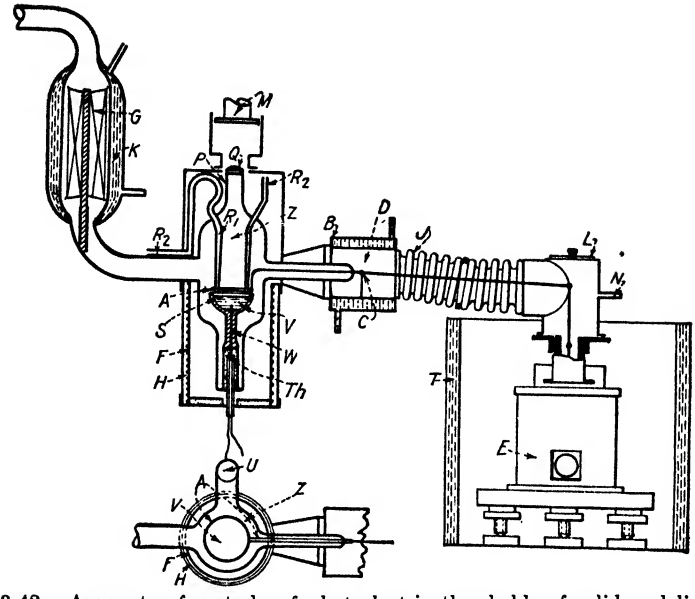

FIG. 3-42.—Apparatus for study of photoelectric thresholds of solid and liquid tin. (*Goetz.*) *V*, glass cup containing tin. *Th*, thermocouple. *W*, tungsten lead making contact with tin. R_1, tube for admission of H_2. R_2, tube for admission of liquid tin. *Q*, quartz window and lens. *M*, exit slit of monochromator. *C*, "hot-wire" pressure gage. *H*, heater coils. *J*, evacuated sylphon tube carrying electrometer lead. *E*, Hoffman electrometer. *A*, anode ring.

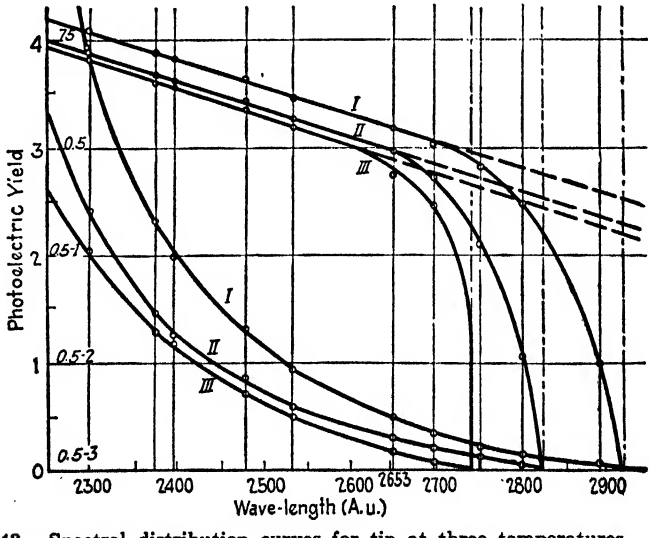

FIG. 3-43.—Spectral distribution curves for tin at three temperatures. (*Goetz.*) I. 400°C (liquid). II. 210°C (γ-crystal form). III. 85°C (β-crystal form). In the upper curves the same data have been plotted on a logarithmic scale.

under a stream of carefully purified H_2 and then in high vacuum until the gage showed no further evolution of gas. The surface was illuminated from above by monochromatic light and the photocurrents collected by an anode consisting of a ring of tungsten wire which had also been thoroughly outgassed. The anode is connected to a wire passing through an evacuated flexible copper tube, which acts as an electrical shield, to a Hoffman electrometer, also evacuated, which is capable of detecting currents as small as 10^{-18} amp. The currents obtained were in all cases extremely small.

Two types of runs were taken. In the first place "isothermal" spectral distribution curves were taken to obtain the threshold at various

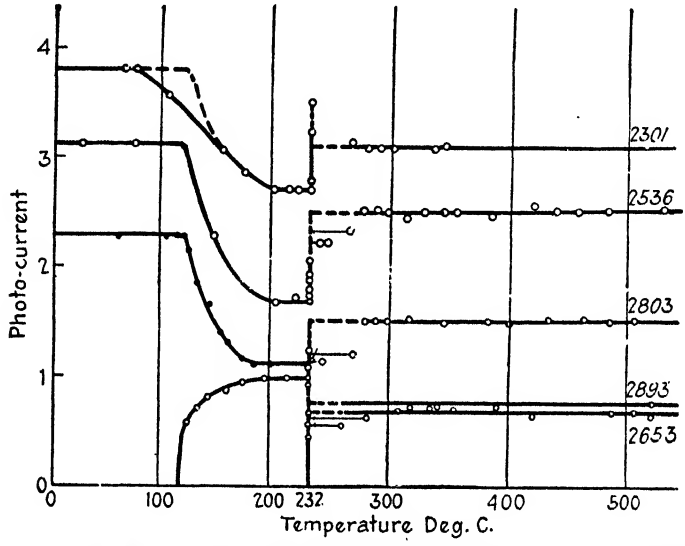

FIG. 3-44.—Variations in the spectral sensitivity of tin during crystal changes. (*Goetz.*) The change from β- to γ-tin takes place at about 120°C, and the melting point is 232°C.

temperatures; secondly, "isochromatic" curves were taken, showing the variation in the photocurrents excited by a single frequency as a function of temperature. Three of the isothermal curves are shown in Fig. 3-43 for three temperatures 85, 210, and 400°C. At 85° the "white" β-crystal form of tin (tetragonal) is stable; at 210° the γ-modification (hexagonal) is obtained, while the 400° curve is for liquid tin, the melting point being 232°C. The thresholds are distinctly different for three phases, the values being 2925A, 2820A, and 2740A, respectively, for the liquid, γ-, and β-forms.

Typical isochromatic curves are shown in Fig. 3-44 for five different wave-lengths. For 2893A the photocurrent remains constant as the liquid tin cools from 500°C to the melting point at 232°, at which point the photocurrent excited by this wave-length suddenly vanishes. This is to be expected, since 2893A is beyond the threshold for γ-tin. For

incident light of wave-length 2803A the curve drops at the melting point to a lower value, then remains constant until the transformation point in the vicinity of 200° is reached, when it begins to decrease and finally vanishes. The change in this case is more gradual, indicating that the crystal transformation itself does not take place suddenly. There is evidence for this from other sources. The wave-length 2803A, it is noted, is beyond the limit for the β-crystal form which is stable below 100°C. If light of a still shorter wave-length be employed the current varies in a different manner. Here the surprising result is obtained that at the γ-β transition, although there is a shift to the *violet* in the threshold, the sensitivity of the surface to light of wave-length shorter than either threshold *increases*, instead of decreasing as is normally the case. It thus appears that the efficiency of emission depends on some other factor characteristic of the surface in addition to the threshold.

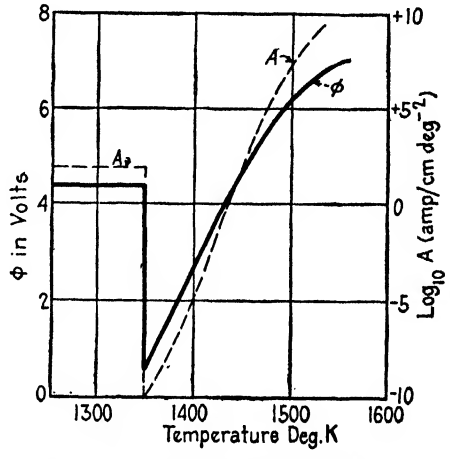

FIG. 3-45.—Variation with temperature of the thermionic work function (ϕ) and constant A for copper in passing through the melting point (1358°K).

The chief point of interest is that it has been definitely established that under the most satisfactory conditions the photoelectric threshold of a surface depends upon its crystal structure. Goetz had previously shown through an equally elaborate series of experiments[1] that the thermionic work function of the metals, copper, silver, and gold, changed sharply in passing through the melting point—the work function for the liquid being always less than for the solid phase. The large decrease in work function at the melting point was always accompanied by a decrease in the factor A in the thermionic equation so that there was *not* a large change in the total thermionic current. Curves showing the work function and the value of A as a function of temperature are shown in Fig. 3-45. Goetz has suggested that there may be a close relation between the constant A and the factor which determines the efficiency of photoelectric emission. A theoretical discussion of the variations of A has been given by Fowler and Nordheim, but no theory of the corresponding photoelectric quantity has been given.

A study of the photoelectric emission from a surface of mercury between room temperature and $-110°$ has recently been made by Miss

[1] A. GOETZ, *Zeits. f. Phys.*, **42**, 329 (1927); **43**, 531 (1927).

Grützmann.[1] There is no variation of photocurrent with temperature throughout this range, even when the specimen passes through the melting point at −40°C. Similar results have been obtained by Roller,[2] so that it appears that the liquid and solid surfaces of mercury have the same threshold.[3]

3-31. Effect of Electric Fields.—The effects of intense electric fields on the photoelectric threshold of thin layers of potassium on tungsten have recently been investigated by Lawrence and Linford.[4] Ives[5] and Suhrmann[6] had both previously reported that photoelectric currents from thin alkali-metal films did not reach saturation even though large accelerating fields were applied. The currents from thick layers, however, saturated quite readily. It is evident that this is the photoelectric analogue of the Schottky effect so well known in thermionic emission. The theory of this effect and its experimental verification are discussed in Sec. **6-15**.

In the experiments of Lawrence and Linford a thin potassium film was deposited on a fine tungsten wire suspended along the axis of a small nickel cyclinder in a thoroughly outgassed tube. Photoelectric spectral distribution curves were taken for a series of values of the accelerating voltage applied to the cylinder. The electric fields at the surface of the filament were in some cases as high as 63,000 volts/cm. A series of curves obtained is reproduced in Fig. 3-46 and it is evident that there is a marked shift in the threshold toward the red with applied field. It was found that the magnitude of the shift is approximately proportional to the square root of the applied field, as would be expected from the Schottky theory if the field holding the electron to the metal surface is principally that due to the image force. As will be pointed out in Sec. **6-15** such investigations offer a powerful method of investigating the nature of surface forces.

Nottingham[7] has studied the variation in the threshold at very small accelerating and retarding fields for a thin film of alkali metal on nickel and platinum. The effective work function for such a surface was observed to decrease by 1.95 volts as the accelerating potential was increased from zero to 4 volts, while an increase to 750 volts caused a further decrease of the work function of only 0.32 volt.

[1] M. Grützmann, *Ann. d. Phys.*, **1**, 49 (1929).

[2] D. Roller, *Phys. Rev.*, **35**, 122 (1930).

[3] Since this section was written a study of the thresholds of single crystals and polycrystalline zinc has appeared by J. H. Dillon, *Phys. Rev.*, **38**, 408 (1931). A carefully degassed zinc single crystal showed a threshold of 3460A when the (0001) face was illuminated. A polycrystalline face exhibited a threshold at 3720A under the same conditions.

[4] E. O. Lawrence and L. B. Linford, *Phys. Rev.*, **36**, 482 (1930).

[5] H. E. Ives, *Astrophys. Jour.*, **60**, 209 (1924).

[6] R. Suhrmann, *Naturwiss.*, **16**, 336 (1928).

[7] W. B. Nottingham, *Phys. Rev.*, **35**, 1128 (1930).

Linford[1] found that for a thoriated-tungsten surface the threshold shifted from 4900A for an applied field of 360 volts/cm to 5500A for an applied field of 48,200 volts/cm. Huxford[2] has reported a shift in the

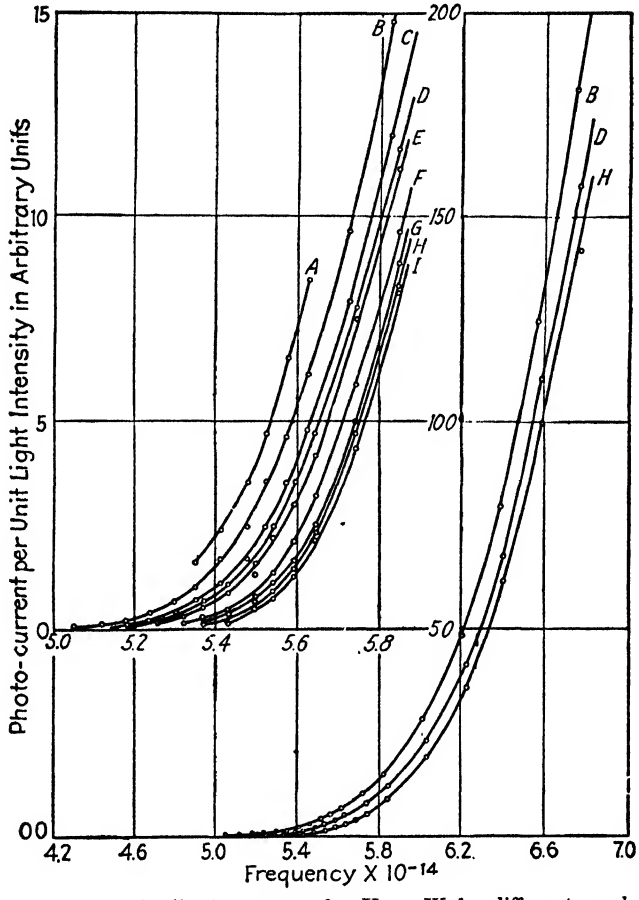

FIG. 3-46.—Spectral distribution curves for K on W for different accelerating fields. At right, three complete curves. At left, nine curves on an enlarged scale. The fields are as follows (in volts/cm) *A*. 63,100. *B*. 36,200. *C*. 22,100. *D*. 15,800. *E*. 9000. *F*. 3100. *G*. 1000. *H*. 260. *I*. 0. (*Lawrence and Linford.*)

threshold of a barium oxide-coated filament from 9200A at a field of 40 volts/cm to 10,800A for a field of 8000 volts/cm.

Thus while the effect of applied field is quite small for clean metal surfaces, it becomes of considerable importance for composite surfaces, and in fact raises the question as to just how the work function of such a surface is to be defined, since some accelerating field must always be applied to collect the electrons.

[1] L. B. LINFORD, *Phys. Rev.*, **36**, 1100 (1930).
[2] W. S. HUXFORD, *Phys. Rev.*, **37**, 102 (1931); **38**, 379 (1931).

3-32. Variations of the Photoelectric Threshold throughout the Periodic Table.—While our knowledge of the photoelectric work functions of the clean metals is as yet too meager to allow a detailed study of the relation between these and other properties of the metal, nevertheless it is of interest to examine the existing data for general relations. The first point of interest in this connection is the question of whether there are systematic variations in the photoelectric thresholds for the metals throughout the periodic table. It is well known that the first elements of

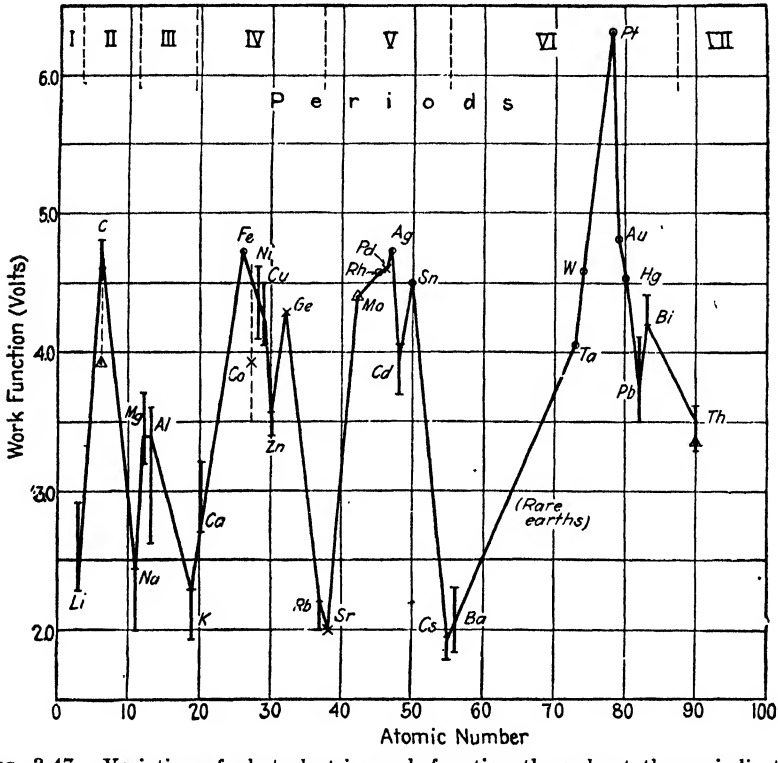

FIG. 3-47.—Variation of photoelectric work function throughout the periodic table. ⊙, values for clean surfaces. ×, single values of uncertain precision. Δ, reliable thermionic value (indicated only when photoelectric value is uncertain). I, vertical lines indicate approximate range covered by various reported values.

each period, the alkalis, have low work functions and there is a general tendency toward higher values as we proceed to metals at the end of the period. Welch[1] has plotted a complete curve for the entire periodic table, and while much of the data is too uncertain to allow conclusions to be drawn, yet such a curve is of considerable interest. In Fig. 3-47 the values of the photoelectric work functions listed in Table 3-2 have been plotted as a function of atomic number. The pronounced minima for the alkali metals are clearly in evidence and there is a pronounced

[1] G. B. WELCH, *Proc. Nat. Acad. Sci.*, **13**, 111 (1927).

maximum in the curve reaching its highest value for Pt. This might point to the expectation that similar maxima will appear for the corresponding elements in the previous long periods, namely nickel and palladium, when their photoelectric properties are more thoroughly studied for surfaces free of contamination.

A recent study of clean Pd (carried out by DuBridge and Roehr since the above was written) shows a value for its work function of 4.96 volts, so that there should be a slight maximum in the curve of Fig. 3-47 at Pd. Similarly a recent study of Ni by Glasoe (*Phys. Rev.*, **38**, 1490 [1931]) gives 5.01 volts for its work function so the curve should reach another maximum at Ni.

It is seen that all the alkali metals show work functions of less than 2.5 volts, with a tendency toward lower values for the heavier members of the group. A similar tendency is evident for the Ca-Sr-Ba sequence, which have work functions ranging below 3.0 volts. The Mg-Zn-Cd-Hg group shows a regular *increase* with atomic number, ranging from 3.5 to 4.5 volts. All the other metals except Pt fall in the range between 3.8 and 5.0 volts and the values are too uncertain to permit discovery of other general tendencies

CHAPTER IV

ENERGY AND SPECTRAL DISTRIBUTION OF PHOTOELECTRONS

I. ENERGY DISTRIBUTION

It was pointed out at the beginning of Chapter III that the velocity distribution function for the photoelectrons emitted from a metal surface is of fundamental importance in a complete description of the photoelectric properties of the surface. This function, Ψ, is defined by the equation,

$$dn = \Psi(\nu,v)dv,$$

where dn is the number of photoelectrons ejected by unit intensity of light of frequency ν, which have the velocity v in the range dv. Closely allied to the velocity distribution function, and of somewhat more direct significance experimentally, is the *energy* distribution function, Φ, defined by the equation,

$$dN = \Phi(\nu,V)dV,$$

where dN is the number of emitted electrons having kinetic energy in the range dV. V will usually be measured in electron-volts.[1] The experimental problems connected with the measurement of energy distribution functions for the purpose of determining the *maximum*

[1] If the function $\Psi(\nu, v)$ is known for a particular value of ν, $\Phi(\nu, V)$ may be calculated by making the substitutions,

$$(\tfrac{1}{2})mv^2 = eV,$$

or

$$v^2 = \frac{2eV}{m},$$

and

$$dv = \left(\frac{e}{mv}\right)dV.$$

Hence, except for constant factors which will not change the *shape* of the distribution curves, we have,

$$\Phi(V) = \left(\frac{1}{v}\right)\Psi(v),$$

and

$$\Psi(v) = V^{\frac{1}{2}}\Phi(V)$$

Thus, if the curve $\Psi(v)$ is plotted as a function of v, the shape of the curve for $\Phi(V)$ as a function of V may be obtained by multiplying the ordinates of the first curve by $1/v$ and plotting them against the square of the corresponding abscissa.

energy of emission and testing the Einstein equation have been discussed in Chapter II. We now take up more in detail the present experimental knowledge of the actual *form* of these distribution functions.

4-1. Methods of Measurement.—There are two general methods of measuring the kinetic energy of photoelectrons emitted from metal surfaces, namely, the magnetic-deflection method and the retarding-potential method. The former method has been employed principally by Ramsauer,[1] Klemperer,[2] and Wolf.[3] One form of apparatus used by Klemperer is shown diagrammatically in Fig. 4-1. It consists of a short cylinder, 16 mm long and 10 mm in radius, closed at each end and divided into partitions as shown. Light entering through the slit releases electrons from the plate B. Under the influence of a magnetic field, perpendicular to the plane of the diagram, they are bent into circular paths, and those having a particular velocity pass through the slits F_1, F_2, and F_3 into the receiving chamber A connected to an electrometer. The number of electrons reaching the receiver is plotted as a function of the magnetic field, and this gives directly a *velocity* distribution curve. Klemperer's apparatus was designed so that the stopping-potential method of analyzing velocities could also be used by applying potentials to the cylinder Z.

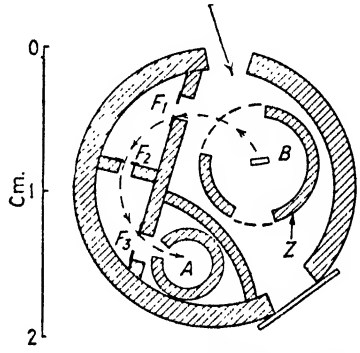

FIG. 4-1.—Apparatus for obtaining velocity distribution of photoelectrons by magnetic deflection. (*Klemperer.*) A. Receiving cylinder. B. Illuminated plate. A retarding potential could be applied to cylinder Z.

There are two factors which limit the accuracy of the results obtainable by the magnetic-deflection method. In the first place, in order to secure measurable currents to the electrometer, it is often necessary to widen the slits to the point where the resolving power of the apparatus is seriously impaired. In the second place it is always possible for electrons of velocities higher or lower than that which the apparatus is set to isolate to reach the receiving electrode by multiple reflection from the walls of the container. As has been pointed out in Chapter II, these difficulties become particularly troublesome when the number of electrons in the main beam passing through the slits is very small, that is, for velocities near zero and near the maximum. Hence the curves obtained can not be relied upon in these regions, though for intermediate velocities they apparently represent the true distribution fairly accurately.

[1] C. RAMSAUER, *Ann. d. Phys.*, **45**, 961 (1914).
[2] O. KLEMPERER, *Zeits. f. Phys.*, **16**, 280 (1923).
[3] F. WOLF, *Ann. d. Phys.*, **83**, 1001 (1927).

In the retarding-potential method of analysis the photoelectric current from a plate is measured as a function of the retarding potential applied between the plate and a receiving electrode. This yields a voltage-current curve of the type which has been discussed in Chapter II, the first derivative of which is the *energy* distribution curve.

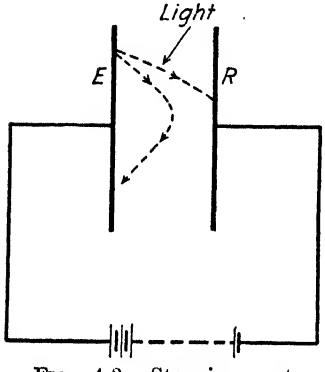

FIG. 4-2.—Stopping potential applied between parallel plates determines the normal component of velocity.

The actual form of the voltage-current curves will depend greatly on the shape and relative position of the receiving electrode and emitting surface, and it becomes of importance to determine under what conditions the *true* energy distribution may be obtained. It is obvious, for example, in the case of the parallel plate arrangement represented in Fig. 4-2, that only the component of the electron velocity which is normal to the receiving plate will be effective in overcoming the retarding field between the receiver R and the emitter E. Hence the distribution curve obtained experimentally will be that of the normal component of the velocity—and this may not remotely resemble the total energy distribution, as we have seen.[1]

The true energy distribution curves may be obtained, however, by using a spherical condenser (central field) in which the electrons are released from a small sphere or plate placed at the center of a larger sphere which acts as a receiver (Fig. 4-3). If the inner sphere is sufficiently small, then all electrons approach the receiving surface normally and the number which reach this outer sphere against a retarding potential V is just the number which actually leave the surface of the inner sphere with a kinetic energy greater than eV. Due to the finite size of the inner sphere, however, all the electrons will not travel exact radial paths, and hence some leaving the surface with kinetic energies slightly greater than eV will fail to reach the surface.[2] In the most precise

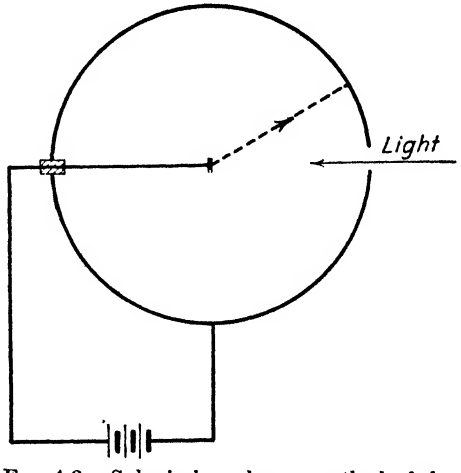

FIG. 4-3.—Spherical condenser method of determining velocity distribution.

[1] See Sec. 2-2.

[2] T. C. FRY and H. E. IVES, *Phys. Rev.*, **32**, 44 (1928).

experiments[1] by this method, however, the dimensions of the spheres were such that all electrons leaving the inner electrode with energies as much as 2 per cent greater than eV would certainly reach the receiving sphere.

The central-field method for obtaining energy distribution curves has been used principally by Richardson and Compton,[2] Herold,[3] and Lukirsky and Prilezaev.[4] In the hands of the last named investigators it was made to yield results of considerable precision.[5] The chief source of error inherent in the stopping-potential method of analyzing electron velocities lies in the fact that in order to obtain energy distribution curves

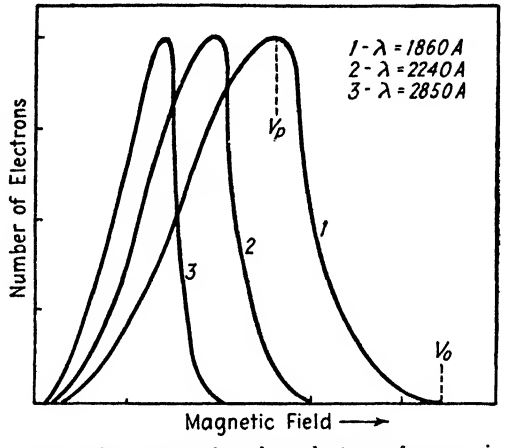

FIG. 4-4.—Velocity distribution curves for photoelectrons from a zinc surface, obtained by magnetic-deflection method. (*Ramsauer.*)

it is necessary to differentiate the observed voltage-current curves—a process which always greatly magnifies any errors in the original observations.

A third method of analyzing electron velocities, making use of a radial electrostatic field in a manner analogous to the way in which the magnetic field is employed in Ramsauer's method, has recently been perfected by Hughes, Rojansky, and McMillen.[6] This method has many important advantages over the two others, but has not as yet been applied to the analysis of photoelectron velocities.

4-2. General Results.—A series of velocity distribution curves for a zinc surface obtained by Ramsauer,[7] using the magnetic-deflection method, are shown in Fig. 4-4. The number of electrons reaching the

[1] P. LUKIRSKY and S. PRILEZAEV, *Zeits. f. Phys.*, **49**, 236 (1928).

[2] O. W. RICHARDSON and K. T. COMPTON, *Phil. Mag.*, **24**, 575 (1912).

[3] F. HEROLD, *Ann. d. Phys.*, **85**, 587 (1928).

[4] P. LUKIRSKY and S. PRILEZAEV, *Zeits. f. Phys.*, **49**, 236, (1928).

[5] Also H. E. IVES and T. C. FRY, *Astrophys. Jour.*, **56**, 1 (1922).

[6] A. L. HUGHES, V. ROJANSKY, and J. H. MCMILLEN, *Phys. Rev.*, **34**, 284 and 291 (1929).

[7] C. RAMSAUER, *Ann. d. Phys.*, **45**, 1124 (1914).

receiving electrode is plotted as a function of the strength of the deflecting magnetic field, which in turn is proportional to the velocity of the electrons. The curves, therefore, represent the function $\Psi(v)$ for various values of the incident wave-length. These curves show very well the general characteristics of the velocity distribution functions, namely: (1) There are some photoelectrons of all velocities from 0 up to a maximum v_0. (2) There is a well-defined most probable velocity v_p. (3) There are relatively few electrons having velocities near zero or near the maximum. (4) In accordance with the Einstein equation the value of the maximum velocity increases with decreasing wave-length.

Ramsauer found that by bringing the most probable velocities into coincidence and by plotting as abscissa the ratio of v to the most probable

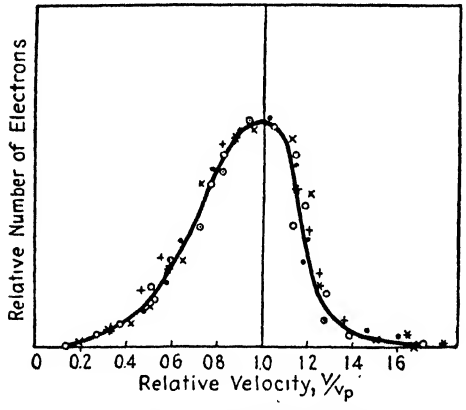

FIG. 4-5.—Composite velocity distribution curve. (Different types of experimental points represent results obtained with different incident wave-lengths.)

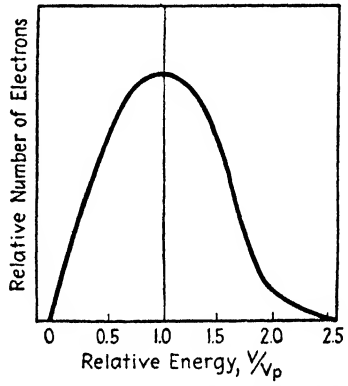

FIG. 4-6.—Composite energy distribution curve. (*Results of Ramsauer, plotted by A. Becker.*)

velocity v_p the curves could all be superposed, as shown in Fig. 4-5. It is seen that the ratio of the most probable velocity to the maximum velocity is a constant and equal to approximately 0.6. If the curves are plotted in terms of the *energy* of emission, the composite curve takes the form shown in Fig. 4-6,[1] from which it can be seen that the most probable *energy* of emission is about 0.4 of the maximum. The figures show the tendency for the distribution curves obtained using the magnetic-deflection method to approach the axis asymptotically in the neighborhood of the maximum velocity, rather than to cut in sharply as do the curves obtained by the stopping-potential method. Klemperer[2] has made a direct comparison in the same apparatus beween the results of the two methods, and the two curves are reproduced in Fig. 4-7. Klemperer attributes the pronounced "foot" of the magnetic-deflection curve to the reflection of low-velocity electrons into the receiving chamber.

[1] A. BECKER, *Ann. d. Phys.*, **58**, 457 (1919).

[2] O. KLEMPERER, *Zeits. f. Phys.*, **16**, 280 (1923).

A typical set of voltage-current curves obtained in a radial field by Richardson and Compton[1] has been reproduced in Fig. 2-8, page 18. Becker[2] found that by bringing the steepest portions of 22 different voltage-current curves of this type (including those obtained by Richardson

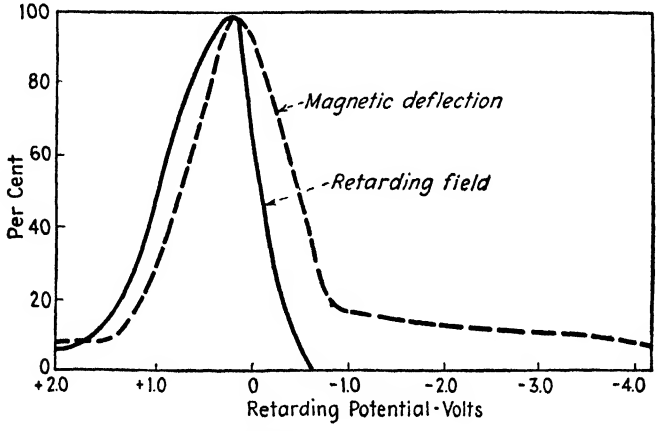

FIG. 4-7.—Comparison of energy distribution curves by magnetic-deflection and retarding-field method. (*Klemperer.*)

and Compton and other observers, for different metals and different wave-lengths) into coincidence, and by plotting as abscissa V/V_p where V_p is the most probable energy, the curves could be completely superposed. The composite curve is shown in Fig. 4-8, the short horizontal lines representing the maximum range of values of the individual curves. The composite Ramsauer curve when integrated also yields a voltage-current curve which fits closely the curve of Fig. 4-8. These results would seem to indicate that there must be a universal function representing the distribution of energy of the emitted electrons from all types of surfaces and for all wave-lengths, though the mathematical form of this function has not been found. The agreement in the shapes of the various curves, however, must be regarded as partly accidental, since more recent work by Bennewitz[3] has shown that the form of the distribution curves varies

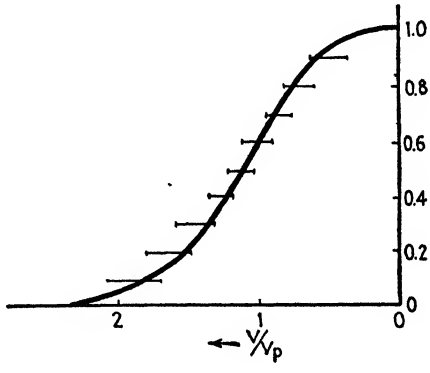

FIG. 4-8.—Composite voltage-current curve for photoelectrons ejected by light and X-rays. (*Becker.*)

[1] O. W. RICHARDSON and K. T. COMPTON, *Phil. Mag.*, **24**, 575 (1912).
[2] A. BECKER, *loc. cit.*
[3] W. BENNEWITZ, *Ann. d. Phys.*, **83**, 913 (1927).

greatly with the state of outgassing of the surface, and very little of the existing data has been taken for surfaces which were thoroughly cleaned of occluded gases.

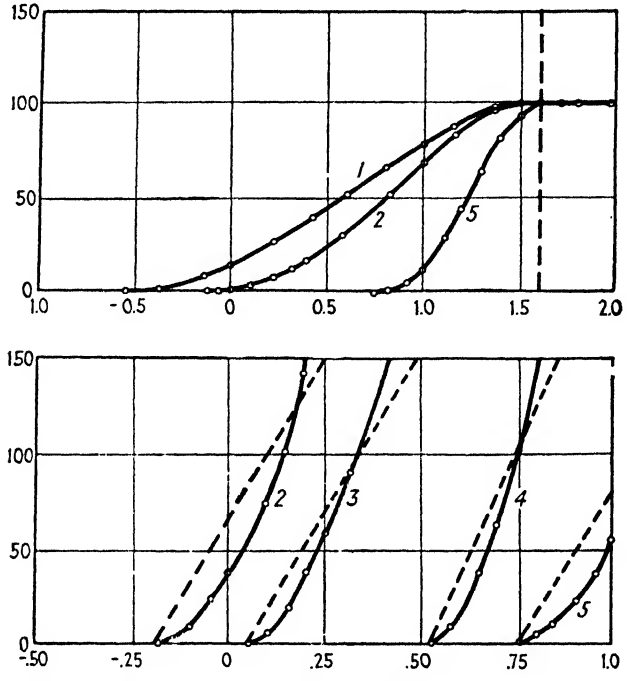

FIG. 4-9.—Voltage-current curves for zinc. (*Lukirsky and Prilezaev.*) Lower figure shows magnified portions near the intercept. The broken straight lines are obtained if $\sqrt{i}$ is plotted against V. 1. λ = 2302A. 2. 2537A. 3. 2653A. 4. 2967A. 5. 3130A.

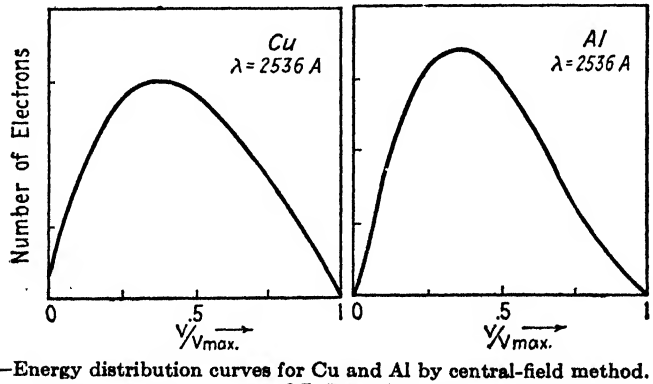

FIG. 4-10.—Energy distribution curves for Cu and Al by central-field method. (*Lukirsky and Prilezaev.*)

The most precise work on the form of the energy distribution functions is that reported by Lukirsky and Prilezaev, who used also the method of central fields, and made a study of several different metals. Their

apparatus and experimental methods have been discussed in Chapter II. A typical set of voltage-current curves for zinc is reproduced in Fig. 4-9, and the derived energy distribution curves for Cu and Al in Fig. 4-10. The maximum energy V_0 is used as an energy unit for the abscissa in the latter curves. It was found that, when plotted in this way, the curves for different wave-lengths practically superpose, but there is some difference in shape between the curves for different metals. The most probable energy is again found to be approximately 0.4 of the maximum.

The question as to the sharpness with which the energy distribution curves plunge into the axis at the maximum energy V_0 is of considerable interest. The curves obtained by the magnetic-deflection method, as we have seen, show an asymptotic approach to the axis which is probably spurious. In the experiments of Millikan[1] and others it was found

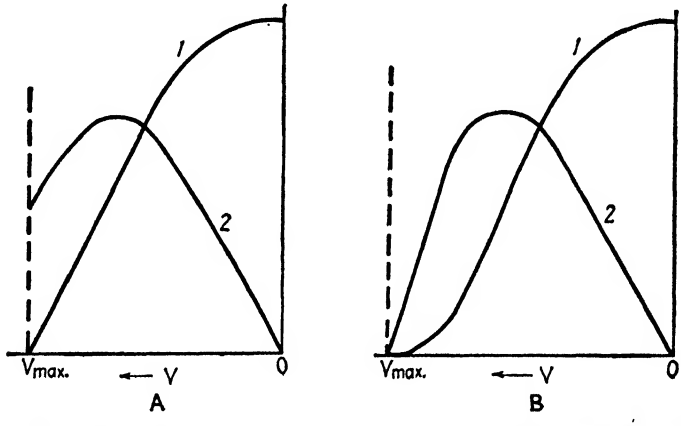

FIG. 4-11.—Two types of voltage-current curves (1), and the corresponding energy distribution curves obtained by differentiation (2).

that the *voltage-current* curves apparently plunged into the axis at a large angle. This result is rather curious, since it means that the corresponding *energy* distribution curve for the photoelectrons must be *discontinuous* at V_0, as shown in Fig. 4-11*A*. If, as seems more likely, the distribution curves are continuous, the voltage-current curves should meet the axis at a zero angle, as suggested by Klemperer and as observed by Lukirsky and Prilezaev (Fig. 4-11*B*). While this distinction is important in principle, the two cases may be indistinguishable experimentally, since there is nothing to prevent the distribution curves from being very steep near V_0, so that the voltage-current curve bends sharply just before touching the axis. (It should be kept in mind, of course, that touching the axis at zero angle is a totally different thing from approaching it asymptotically.) As a matter of fact, the Sommerfeld theory of electrons in metals predicts, as pointed out by Fowler, that the distribution curves

[1] R. A. MILLIKAN, *Phys. Rev.*, 7, 355 (1916).

should be very steep near V_0 but should actually be discontinuous only at the temperature 0°K.

4-3. Effect of Direction of Emission.—The effect on the velocity distribution curves of the direction in which the electrons emerge from the surface and the direction of the incident light has been studied for solid metals and, with still more interesting results, for thin metal films.

For *solid metals* Ramsauer[1] studied the velocity distribution curves of the electrons emerging normal to the surface and of those emerging at an angle of 45 deg, using a brass cathode and the unresolved light from a mercury arc. The two curves coincided within the limits of error and neither curve was affected when the angle of incidence of the light was changed from 0 deg to 45 deg. From this it may be concluded that the velocity distribution of photoelectrons emitted from a metal surface does not depend on the direction of ejection or the angle of incidence of the light, at least as long as these are within 45 deg of the normal.

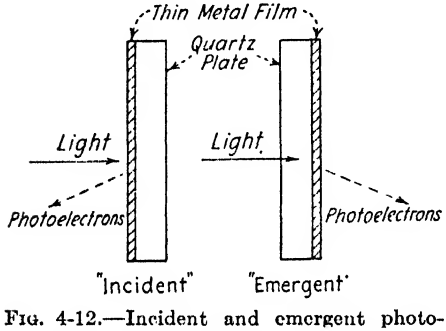

FIG. 4-12.—Incident and emergent photoelectric effects from thin metal films.

In 1907 Rubens and Ladenburg[2] found that when *thin transparent films* of metal deposited on quartz were illuminated by light, the photoelectric currents from the metal surface were greater when the light was incident on the side next to the quartz than when the metal film was directly exposed[3] (Fig. 4-12). Robinson[4] and Stuhlmann[5] reported that not only were the currents greater from the *emergent* side of the film than from the *incident*, but

[1] C. RAMSAUER, *Ann. d. Phys.*, **45**, 961 (1914).

[2] H. RUBENS and E. LADENBURG, *Verh. d. Deutsch. Phys. Ges.*, **24**, 749 (1907).

[3] Similar results were found by Kleeman (*Proc. Roy. Soc.*, London, **84**, 92, [1910]) and Stuhlmann (*Phil. Mag.*, **20**, 331 [1910]; **22**, 854 [1911]). It was thought at first that this was due to a tendency of the electrons to be ejected more copiously in the direction of the incident light. However, Partzsch and Hallwachs (*Ann. d. Phys.*, **41**, 247 [1913]) showed that this asymmetry in *number* of electrons could be adequately accounted for in terms of the optical properties of the films, principally the difference in reflectivity of the quartz-metal and vacuum-metal surfaces. In the case of electrons ejected from thin films by X-rays, however, there is a real asymmetry in the number of electrons emerging from the two sides of the film, more electrons being ejected from the emergent side. This effect is due to the transfer of the momentum of the incident quanta to the electrons, but is inappreciable for visible and ultraviolet light. The *maximum energy* of emission is in all cases accurately independent of the direction of the incident radiation, as required by the Einstein equation.

[4] J. ROBINSON, *Phil. Mag.*, **25**, 115 (1913).

[5] O. STUHLMANN, *Phys. Rev.*, **4**, 195 (1914).

the maximum velocity of emission was also greater. This result aroused considerable interest, since the electrons in the two cases were actually being released from the same surface, by light of the same frequency, and hence a difference in the maximum velocities would mean a failure of the Einstein equation, *i.e.*, a difference in the value of h for the two directions of emission. The ratio of emergent to incident velocities was found to be as great as 1.3 in some cases, but decreased with increasing thickness of film, actually becoming less than unity for films of thickness greater than 10^{-7} cm. For these thicker films the *number* of electrons from the emergent side was also less, owing to the fact that all the light did not penetrate through the film to the emitting surface.

Piersol[1] in 1924 examined this question with great care and found that the apparent asymmetry in velocities was due to the presence of scattered light of short wave-length, and when this was eliminated by filters, the voltage-current curves taken for the two directions of the incident light plunged into the axis at the same point. Figure 4-13 shows the type of apparatus used in all these investigations, and Fig. 4-14 shows Piersol's curves taken with and without filters to cut out stray light. Piersol's procedure differed from that of his predecessors in that to eliminate gases from his films of platinum he deposited them by evaporation in high vacuum instead of by cathode sputtering. Chien Cha[2] later used both types of film in the same apparatus and confirmed Piersol's results for the evaporated films, but found an apparent asymmetry in the emission velocities for films sputtered in an atmosphere of hydrogen. More recently, Herold[3] has found, however, using the method of central fields, that even for sputtered films the velocity-distribution curves are completely independent of the direction of the incident light, and the curves for the incident and emergent electrons can in fact be superposed, as shown in Fig. 4-15.[4] Experiments with X-rays[5] confirm those with ultra-violet light, and point to the general conclusion that emission velocities of electrons ejected from metal surfaces are independent of the direction of the incident light—a result wholly in agreement with the quantum-theory viewpoint of the process.

4-4. Effect of Film Thickness.—Two investigations have been reported in which the form of the velocity distribution function has been studied as a function of the thickness of the film of metal from which the photoelectrons were emitted. In both cases it was found that the form of the curves remained independent of the thickness until it was reduced to some critical value, below which the curves showed a progres-

[1] R. J. Piersol, *Phys. Rev.*, **23**, 144 (1924).
[2] Chien Cha, *Phil. Mag.*, **49**, 262 (1925).
[3] F. Herold, *Ann. d. Phys.*, **85**, 587 (1928).
[4] F. Herold, *loc. cit.*
[5] W. Seitz, *Phys. Zeits.*, **25**, 546 (1924); E. C. Watson, *Phys. Rev.*, **30**, 479 (1927).

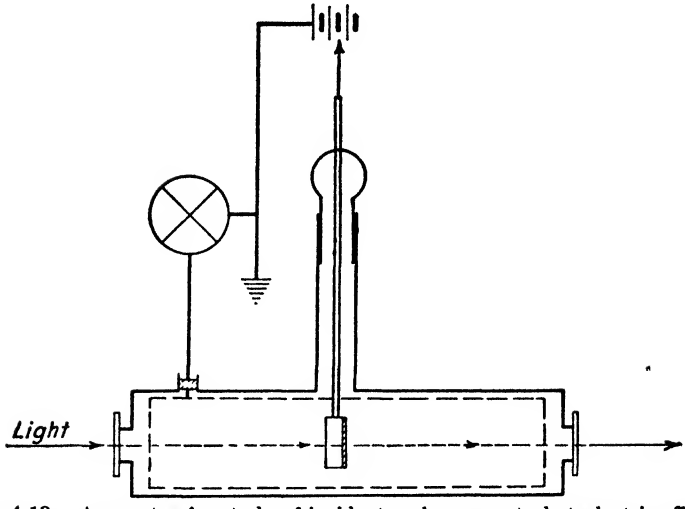

FIG. 4-13.—Apparatus for study of incident and emergent photoelectric effects.

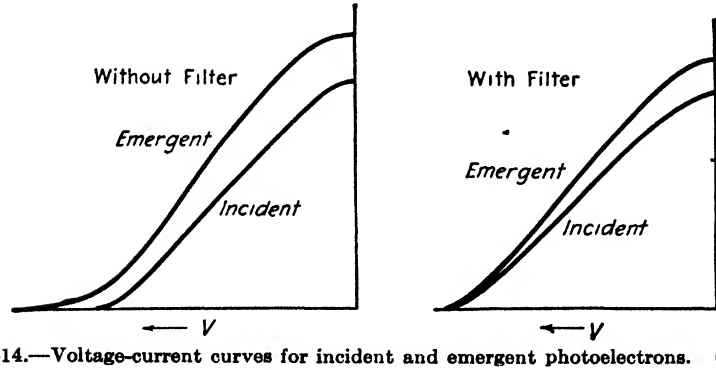

FIG. 4-14.—Voltage-current curves for incident and emergent photoelectrons. (*Piersol.*)

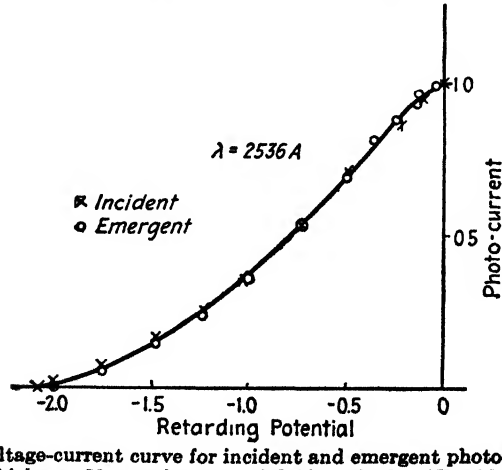

FIG. 4-15.—Voltage-current curve for incident and emergent photoelectric effects from tungsten films of thickness 20$\mu\mu$, using central-field method. (*Herold.*) The curves have been adjusted to the same saturation current.

sive change in form. Figure 4-16 shows a series of curves obtained by Lukirsky and Prilezaev[1] for thin films of silver deposited on glass, using the method of central fields. The curves for the thinner films are characterized by the great decrease in the relative number of low-velocity electrons, by the increase in the sharpness of the maximum, and by the shift of the most probable velocity to higher values. In other words, for thin films the emitted electron beam is more nearly "monochromatic." The critical film thickness was found to be of the order of

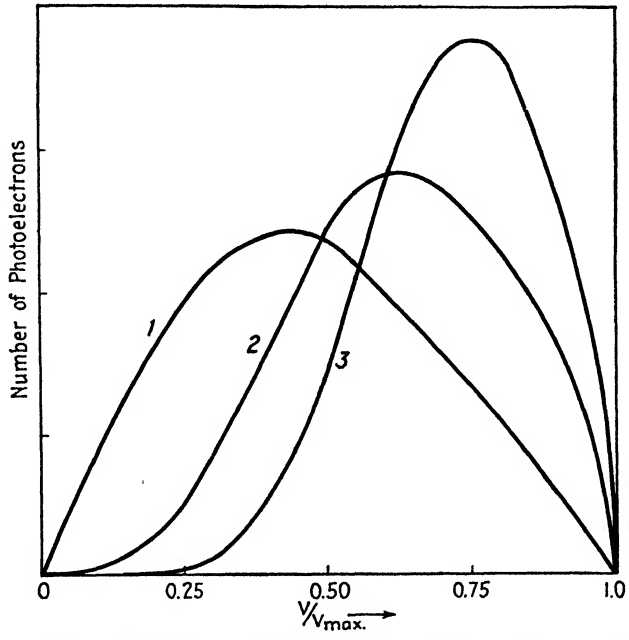

FIG. 4-16.—Energy distribution of photoelectrons from thin films of silver on glass. (*Lukirsky and Prilezaev.*) 1. Thick layer. 2. Film $\sim 3 \times 10^{-6}$ cm thick. 3. Film $\sim 10^{-6}$ cm thick.

5×10^{-6} cm. Similar curves have been obtained by Herold[2] for platinum films on quartz, except that for this metal the critical thickness was found to be ten times smaller. This difference between the two experiments may be partly due to experimental error in measuring the thickness and partly to an actual difference between Ag and Pt films. The critical thickness may be taken as roughly equal to 100 atomic layers.

This change in the form of the velocity distribution curve with film thickness may be most easily interpreted by assuming that in thin films the electrons, after absorbing the incident quanta, need travel only a short distance before reaching the surface layer and hence suffer fewer energy losses by collision. A larger percentage of the electrons

[1] P. LUKIRSKY and S. PRILEZAEV, *Zeits. f. Phys.*, **49**, 236 (1928).
[2] F. HEROLD, *Ann. d. Phys.*, **85**, 587 (1928).

will therefore emerge with velocities near the maximum. As the film thickness is increased, electrons reach the surface from greater depths, and hence with smaller velocities. With still greater thicknesses, however, the number of electrons which can reach the surface from the greater depths becomes negligibly small, and the curves take on the form observed for the massive metal. The critical thickness is therefore a measure of the depth of the photoelectrically active layer of the metal. That this turns out to be about 100 atoms deep is in agreement with the Sommerfeld theory of electrons in metals, according to which the electron mean free path is of about this order of magnitude.[1] Since metal films 10^{-6} cm thick are still quite transparent to ultra-violet light,[2] it is evident that the thickness of the photoelectrically active layer is limited, not by the depth to which light can penetrate, but by the depth from which electrons are able to emerge.[3]

The above conclusions lose much of their force, however, in view of the experiments of Ives,[4] who found the effects of thickness on the voltage-current curves for thin films of alkali metal (potassium) to be the same, whether deposited on tungsten or on glass. Since in the former case most of the photoelectrons probably come from the underlying metal, the thickness of the alkali-metal film bears no direct relation to the depth from which the photoelectrons emerge. It is probable, therefore, that an explanation of the change in the shape of the voltage-current curves is to be found in the fact that films of different thickness produce different types of electric fields in the immediate vicinity of the active surface, possibly due to the fact that in the thinner films a greater fraction of the atoms are adsorbed on the surface as ions.[5]

4-5. Effect of Gases.—The effect of gas layers on the form of the velocity distribution curves has been studied in recent years by Bennewitz,[6] Kluge,[7] and Herold,[8] with results which are in substantial agreement. It has been found that during any changes in gas content of a surface, the maximum velocity of emission, the most probable velocity, the photoelectric threshold, and the contact potential of the surface all shift together in the manner to be expected from the Einstein equation.

[1] Recent work of Ives (*Phys. Rev.* **38**, 1209 [1931]) suggests that the photoelectrically active layer is *much thinner* than this. This view is also suggested by the theoretical work of Tamm and Schubin. See Sec. **6-26**.

[2] Silver films 10^{-6} cm in thickness transmit approximately 75 per cent of the incident light of wave-length 3000A, while gold films of the same thickness transmit 52 per cent and platinum films about 40 per cent. See "International Critical Tables," Vol. V, p. 255. (McGraw-Hill Book Company, Inc.)

[3] This point will be more fully discussed in Chap. XIV.

[4] H. E. Ives, *Astrophys. Jour.*, **60**, 209 (1924).

[5] See Sec. **3-25**.

[6] W. Bennewitz, *Ann. d. Phys.*, **83**, 913 (1927).

[7] J. Kluge, *Ann. d. Phys.*, **82**, 437 (1927).

[8] F. Herold, *Ann. d. Phys.*, **85**, 587 (1928).

The form of the velocity distribution curves depends very greatly on the gas content of the surface, as is shown in Fig. 4-17, which shows four curves taken during successive stages in the process of removing the gas from a strip of platinum foil by heating. The maximum emission velocity shifts first to greater, then to smaller values, corresponding to the changes in the threshold. The low-velocity electrons are relatively more numerous in the curves for the gas-filled specimen—as if the gas layer caused a general loss in energy of the electrons passing through it on their way out. For a degassed specimen there are apparently fewer energy losses by collision, hence the velocities are more closely grouped about the most probable velocity, and this peak occurs at a point about 0.8 of the maximum velocity. The effects observed, however, are very complex and not easily accounted for, and in no case were curves obtained for *thoroughly* cleaned platinum.

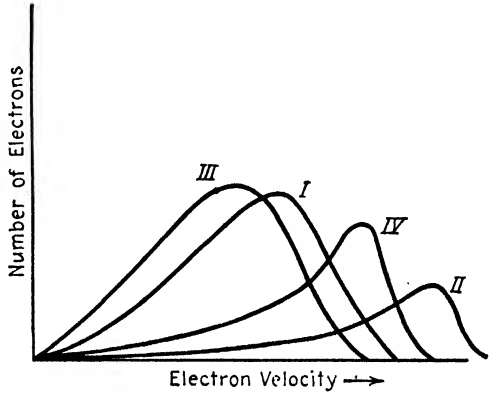

FIG. 4-17.—Effect of gases on the velocity distribution of photoelectrons from Pt for λ2536. I. Fresh specimen. II. After 2 hr of heating in vacuum. III. After standing 15 hr in O_2 at 60 mm pressure. IV. After further heating in vacuum. (*Bennewitz.*)

4-6. Effect of Polarization of the Light.—The question as to whether the distribution of velocities among the emitted photoelectrons was affected by the state of polarization of the incident light has been investigated by a number of observers. Hughes[1] found that the shape of the voltage-current curves varied according to whether the light was polarized in, or perpendicular to, the plane of incidence. This effect, however, was found to be due, not to a difference in the *energy* distribution, but to a difference in the *directional* distribution of the electrons. It was found that the number of electrons coming off at small angles with the normal to the surface was greater when the incident light was polarized with the electric vector parallel to the plane of incidence ($E\|$) than when it was perpendicular to this plane ($E\perp$). It is evident that since the ordinary retarding-potential method, using parallel plates, measures only the distribution of the normal components of velocities, it is incapable of distinguishing directly between changes in energy and in direction (*i.e.*, angular) distribution.

In an extensive investigation to be discussed in detail in the next section, Ives, Olpin, and Johnsrud[2] confirmed Hughes' conclusion that

[1] A. L. HUGHES, *Phil. Mag.*, **31**, 100 (1916).

[2] H. E. IVES, A. R. OLPIN, and A. L. JOHNSRUD, *Phys. Rev.*, **32**, 57 (1928).

there is a greater concentration of electrons in the vicinity of the normal for the case of $E\|$, but that the energy distribution is independent of the polarization of the light. They were able to separate the two effects by using the central-field method and measuring the number of electrons

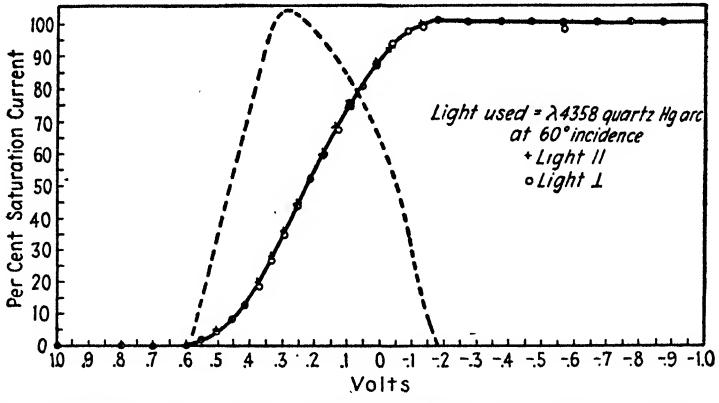

FIG. 4-18.—Voltage-current curve for sodium-potassium alloy, using E‖ and E⊥ light. (*Ives, Olpin, and Johnsrud.*) Broken curve represents the corresponding energy distribution.

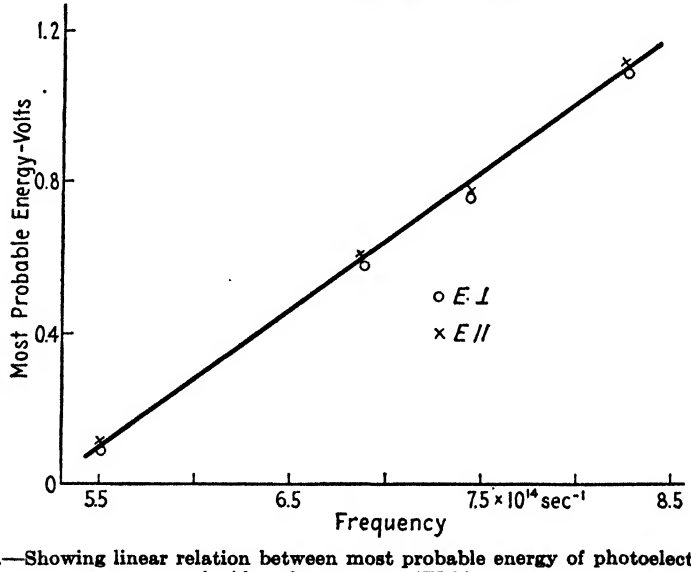

FIG. 4-19.—Showing linear relation between most probable energy of photoelectrons and incident frequency. (*Wolf.*)

reaching a small region on the outer sphere when a small portion of the inner sphere is illuminated. As is seen in Fig. 4-18 the shape of the voltage-current curve obtained in this way is independent of the plane of polarization of the light.

Wolf[1] analyzed by means of the magnetic-deflection method the velocity distribution of the photoelectrons ejected in a given direction

[1] F. WOLF, *Ann. d. Phys.* **83**, 1001 (1927).

(normal to the surface) from Na-K alloy. He found that the distribution curves were unaffected by a change in the plane of polarization of the light, and, in particular, that the most probable velocity of emission is accurately the same for the two cases, $E\|$ and $E\perp$. Furthermore, as shown in Fig. 4-19, there is found to be a linear relation between the most probable energy and the frequency, as would be expected if the most probable energy is always a definite fraction of the maximum energy.

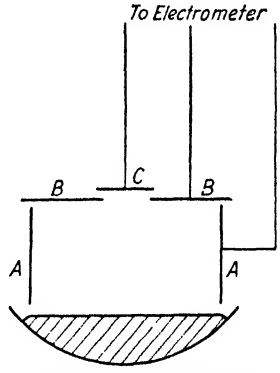

FIG. 4-20.—Apparatus for investigating the directional distribution of photoelectrons.

4-7. Directional Distribution of Photoelectrons.—It is well known[1] that when X-rays eject electrons from atoms there is a strong tendency for the electrons to emerge with an initial velocity in the direction of the electric vector of the (polarized) X-ray beam. It is of interest to inquire whether the same effect is to be observed for the electrons emerging from a metal surface under the influence of ultra-violet light. Hughes[2] investigated the question qualitatively, using the apparatus shown in Fig. 4-20. The electrons ejected from the metal surface could be collected by an anode which was in three parts, the cylinder AA, the large plate BB, and the small plate C. The total current could be measured by connecting all three electrodes to the electrometer, while if plate C alone were connected, only the electrons coming off nearly normal to the surface could be observed. It was found that the ratio of the current to C alone to the total current was slightly greater for $E\|$ than for $E\perp$ light.

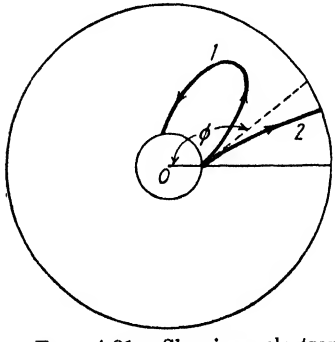

FIG. 4-21.—Showing electron paths in field between concentric spheres. 1. Outer sphere negative (ellipse). 2. Outer sphere positive (hyperbola).

The problem has been more carefully studied by Ives[3] and his co-workers in one of the most beautiful and elaborate experimental investigations in the whole field of photoelectricity. Fry and Ives first computed theoretically the form of the voltage-current curve to be expected when electrons with a given velocity and direction distribution are emitted from a limited region of a small spherical

[1] A. H. COMPTON, "X-Rays and Electrons" (D. Van Nostrand Company). A further discussion of the X-ray data will be found in Sec. **11-7**.

[2] A. L. HUGHES, *Phys. Rev.*, **10**, 490 (1917).

[3] T. C. FRY and H. E. IVES, *Phys. Rev.*, **32**, 44, (1928); H. E. IVES, A. R. OLPIN, and A. L. JOHNSRUD, *Phys. Rev.*, **32**, 57 (1928).

cathode and collected at various points of a larger spherical anode (Fig. 4-21). Since the electric field between the two spheres is simply of the central inverse square type, the paths of the electrons will be portions of conic sections with one focus at the center O. When the outer sphere is negative with respect to the inner (retarding field) the force on the electrons will be toward the center and the paths will be portions of ellipses. When the outer sphere is positive (accelerating field) the paths will be hyperbolic. The two cases are illustrated in Fig. 4-21. Since the equation of the path is well known in either case, it is at once possible to compute, for any value of the potential difference between the two spheres, the velocity which an electron must have such that, leaving the inner sphere at some angle ϕ, it will strike the outer sphere at some point C (Fig. 4-22). Denote the square of this velocity by v^2. Then v^2 will be a function of ϕ and of α, the angular position of C. If the electrons are collected by a zone on the outer sphere of angular width $d\alpha$ then there will be a range of permissible velocities, $(dv^2/d\alpha)d\alpha$. Let I_0 be the total number of electrons released from the inner sphere and let $p(\phi)d\phi$ represent the fraction of these which start off at the angle ϕ in the range $d\phi$. Of these, let $p_\phi(v^2)dv^2$ be the fraction which have the proper velocities to reach the collecting zone. Then the number of these electrons reaching the zone is $I_0p(\phi)d\phi p_\phi(v^2)dv^2$, or, in terms of α, $I_0p(\phi)d\phi p_\phi(v^2)(dv^2/d\alpha)d\alpha$. Since the area of the zone is $2\pi b^2 \sin\alpha\, d\alpha$, the total current per unit area of the zone is,

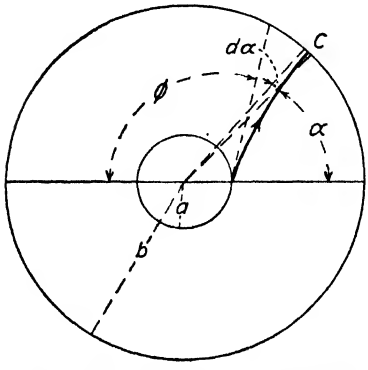

FIG. 4-22.—Motion of photoelectron in central force field, illustrating theory of Ives and Fry.

$$i = \left(\frac{I_0}{2\pi b^2 \sin\alpha}\right)\int p(\phi)p_\phi(v^2)\left(\frac{dv^2}{d\alpha}\right)d\phi, \tag{4-1}$$

the integration being extended over all values of ϕ for which electrons can actually reach C. The integral can be computed, if the functions $p(\phi), p_\phi(v^2)$, and v^2 are known. It was assumed that the directional distribution could be represented by Lambert's law, *i.e.*,

$$p(\phi) = -2 \sin\phi \cos\phi, \tag{4-2}$$

and that the velocity distribution could be represented by an empirical equation which had previously been found[1] to fit the experimental results, namely

$$p_\phi(v^2) = \left(\frac{6}{v_m^2}\right)\left[\left(\frac{v^2}{v_m^2}\right) - \left(\frac{v^2}{v_m^2}\right)^2\right], \tag{4-3}$$

v_m being the maximum velocity of emission.

[1] H. E. IVES and T. C. FRY, *Astrophys. Jour.*, **56**, 1 (1922).

The function $v^2(\alpha,\phi)$ was computed from the equation of the path and involves a and b, the radii of the inner and outer spheres; V, the potential difference between the spheres (chosen to be negative when the outer sphere is positive); and V_0, the maximum emission energy in

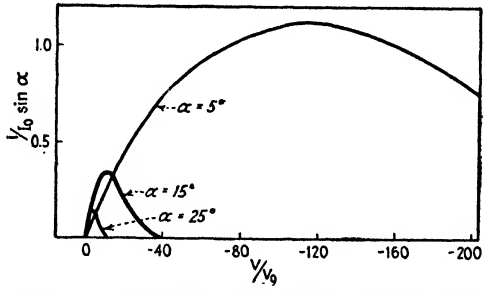

FIG. 4-23.—Total current to collecting zones at various angles α from the normal to the illuminated cathode. (*Ives and Fry.*)

volts. The integral of Eq. (4-1) was evaluated and in Fig. 4-23 the calculated (ratio i/I_0) sin α is plotted as a function of V/V_0 for several chosen values of α. In Fig. 4-24, i/I_0 is plotted in polar coordinates as a

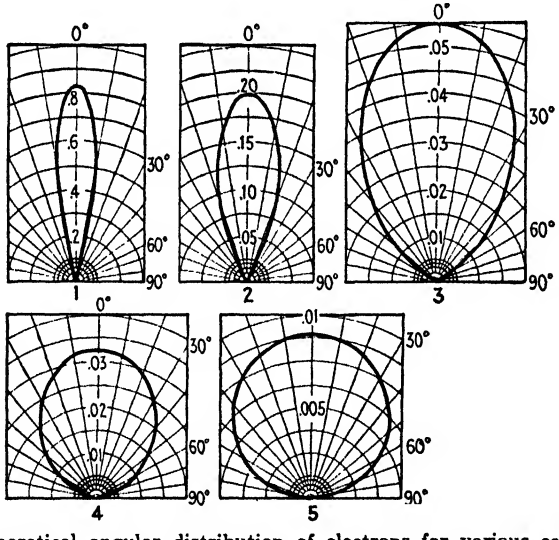

FIG. 4-24.—Theoretical angular distribution of electrons for various cathode voltages. (*Ives and Fry.*) The values of V/V_0 are: 1. -30. 2. -5. 3. $-\frac{1}{2}$. 4. 0. 5. $+\frac{1}{2}$.

function of α for several values of V/V_0. It was assumed in the computations that $b/a = 6$, a value approximated in many of the experiments.

In the experimental work 11 different photoelectric cells were used, all designed to approximate as closely as possible the conditions assumed in the theory. In some of the cells the electrons were collected by a vane moving in the plane of incidence and which could be set at various

positions along a slit in the outer sphere. In other cells the currents were

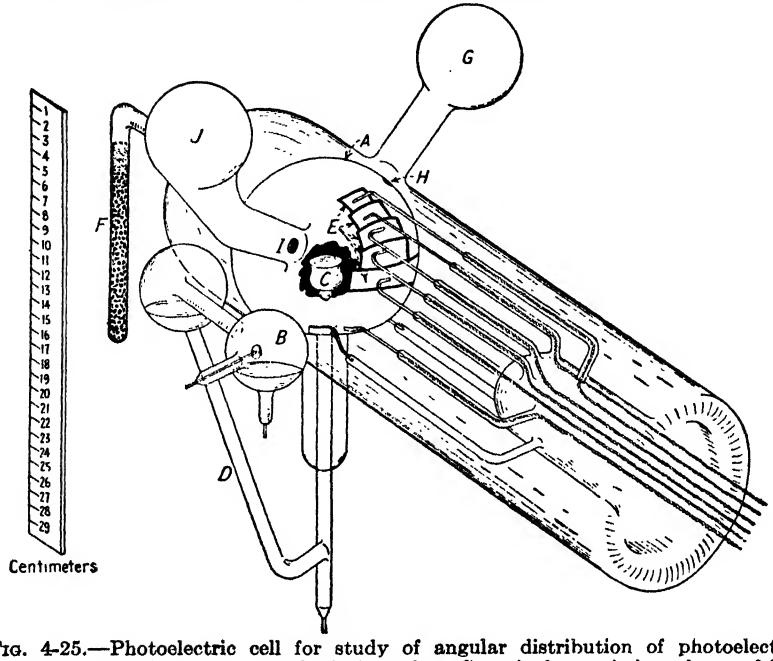

FIG. 4-25.—Photoelectric cell for study of angular distribution of photoelectrons. (*Ives, Olpin, and Johnsrud.*) *A*, spherical anode. *C*, cathode consisting of cup of Na-K alloy. *B*, reservoir for alloy. *G*, bulb for entrance of light *J*, absorbing bulb for light reflected from *C*. *E*, isolated collecting tabs. *F*, charcoal tube.

collected by a series of fixed tabs which formed portions of zones in the outer sphere, but which were insulated from it and from each other. Such a cell is shown in Fig. 4-25. The inner electrode was in some cases a metal sphere coated with alkali metal, in other cases a coated plate, and, for the experiments on liquid Na-K alloy, a small cup, as shown in the figure. It was necessary to coat the outer sphere with soot to prevent formation of an active layer of alkali metals on it, which would give rise to large return currents owing to scattered light. When all spurious effects had been eliminated, the experimental curves of i/I_0 against V/V_0 were found to agree closely with those predicted by the theory (Fig. 4-26). The differences between the observed and cal-

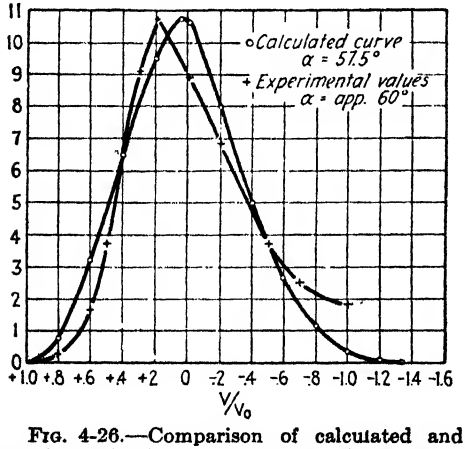

FIG. 4-26.—Comparison of calculated and experimental voltage-current curves for α = app. 60°. $E \parallel$ light incident at 60°; λ = 4358A.

culated curves can be accounted for by the finite width of the collecting tab. The general shape of the curves, though not their absolute magnitude, was independent of the plane of polarization of the incident light. The results of an exhaustive study of the angular distribution curves may be summarized briefly as follows:

1. The distribution of electrons emerging from a metal surface is *always* symmetrical about the normal to the surface, regardless of the angle of incidence or plane of polarization of the incident light.

2. The concentration about the normal is greater in the case of $E\|$ than in the case of $E\perp$ light, and is still less for $E\perp$.[1] The experimental curves are shown in Fig. 4-27.

3. For $E\perp$ light the angular distribution of the electrons emerging in any plane is unchanged when the plane of polarization of the light is rotated.

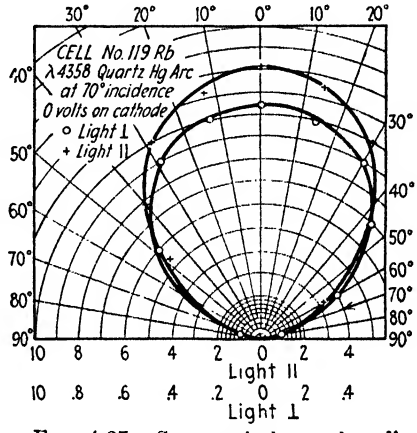

FIG. 4-27.—Symmetrical angular distribution of photoelectrons from Rb, showing no tendency to follow the electric vector. Arrow shows direction of incident light.

These results are of considerable interest in their bearing on the question of whether the photoelectrons ejected by ultra-violet and visible light tend to come off in the direction of the electric vector of the light. The result 1, above, at first sight seems to eliminate this possibility, for if there were such a tendency one would expect that for $E\|$ light at oblique incidence there would be an excess emission in a direction at right angles to the light beam. No trace of this was found. But Fry[2] has shown that in reality this should not be expected, since after the beam enters the metal it is no longer plane polarized, but the electric vector rotates as in elliptically polarized light (although the magnetic vector does not). The major and minor axes of the ellipse, moreover, are not inclined to the surface, but are, respectively, nearly parallel and normal to it, regardless of the angle of incidence. This means that a symmetrical distribution about the normal is still to be expected.

Result 3 definitely shows, however, that when the electric vector is *parallel* to the surface there is *no* tendency for the electrons to follow its direction. On the other hand, if the electric vector has a component *normal* to the surface, then there *is* a tendency for the electrons to show a greater concentration about the normal, as is shown by result 2.

[1] This symbol is used to represent polarized light at *normal* incidence.

[2] T. C. FRY, *Jour. Opt. Soc. Amer.*, **15**, 137 (1928); **16**, 1 (1928).

4-8. Theory of Velocity Distribution.—It will be recalled that the Einstein equation

$$(\tfrac{1}{2})mv_m^2 = h\nu - \phi e$$

gives only the maximum velocity of emission of the photoelectrons, though actually the number of electrons emerging from a surface with the maximum energy is vanishingly small. It is a problem of some importance to account for the actual distribution of velocities observed.

The fact that most of the electrons emerge with velocities less than the maximum may be accounted for in one or more of the following ways:

1. The electrons, assumed to be initially *free*, all absorb the same energy from the incident light and lose the same energy in penetrating the surface layer, but are released from varying depths in the metal and hence suffer varying energy losses in making their way to the surface.

2. The electrons, assumed initially *bound*, lose different amounts of energy in escaping from the parent atoms.

3. The electrons within the metal, before they absorb the incident light, do not all have the same velocity and hence there will be a corresponding distribution of velocities among the emerging electrons.

It will be seen that these three factors are not mutually exclusive, and the observed distribution may be due to a combination of any two or of all three. The best evidence at present, however, seems to indicate that the photoelectrons, for the most part, come from the *free* electrons within the metal, and hence condition 2 probably plays a negligible rôle.

The problem of computing quantitatively the velocity distribution of the emitted electrons on the basis of the above assumptions has not been satisfactorily solved. It is closely related to the whole problem of electron conduction in metals, which will be discussed more in detail in Chapter VI. We may simply mention here for reference that the distribution of the *normal component* of the electron velocities has been worked out on the basis of the first assumption above, in conjunction with the classical theory of electrons, by J. J. Thomson.[1] He obtained the following expression for the rate at which electrons arrive at a collecting plate from a parallel emitting plate whose threshold frequency is ν_0 and which is illuminated by light of frequency ν,

$$R = B\left[1 - \frac{(h\nu_0 + Ve)}{h\nu}\right]^2, \tag{4-4}$$

where B is a constant and V the potential difference between the two plates. The voltage-current curve and the derived distribution curve would then be, respectively, the parabola and the straight line shown in Fig. 4-28. These are not of the type usually observed experimentally, though they seemed to fit some observations made by Thomson himself.

[1] J. J. Thomson, *Phil. Mag.*, **2**, 674 (1926).

On the other hand, R. H. Fowler[1] has shown that on the basis of the Sommerfeld electron theory of metals the distribution is to be accounted

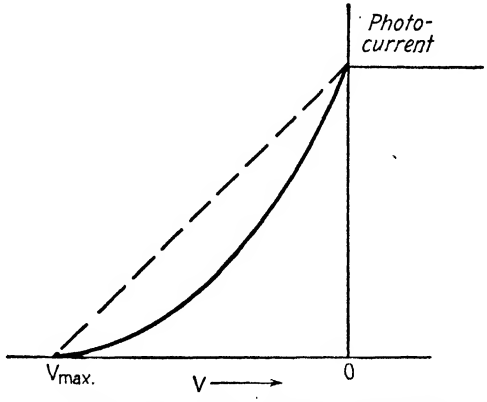

FIG. 4-28.—Theoretical voltage-current and energy distribution curves. (*Thomson.*)

for primarily on the basis of the third factor listed above, and the curves thus predicted are of the same general form as those observed.

II. THE SPECTRAL DISTRIBUTION FUNCTION

Accurate measurements on clean metal surfaces of the photoelectric current per unit intensity of absorbed light as a function of the wave-length or frequency have been made in only a few cases and usually over a relatively limited spectral region. Consequently there is much to be learned as to the nature of spectral distribution functions and how they depend on the nature of the surface. The problem is of considerable importance in several respects. In the first place it is well known that in the surface photoelectric effect, "quantum equivalence" (*i.e.*, the release of one electron for each quantum of light absorbed) is never attained; in fact, seldom is the photoelectric yield ever as great as 1 per cent of quantum equivalence. Thus if within the metal every quantum is absorbed by an electron, as experiments on photoconductivity seem to show, most of the electrons are unable to leave the surface, and the number which does leave depends greatly on the wave-length of the light absorbed. It would be of considerable theoretical importance if the nature of this dependence were known for all surfaces.

Furthermore, a knowledge of the spectral distribution function is of importance from a purely practical standpoint, since the photoelectric sensitivity of various surfaces to a given source of light can be determined only when the distribution functions for the different surfaces are known. Also, the photoelectric thresholds can be most easily determined by extrapolation of the spectral curves to zero current. In the following sections we take up our experimental knowledge of such curves.

[1] R. H. FOWLER, *Proc. Roy. Soc.* **122**, 36 (1929).

4-9. Experimental Results.—The type of curve exhibited by a surface depends on the nature of the surface and the state of polarization of the light. Curves of the type *B*, Fig. 4-29, (known as the "normal" curves) are shown by many metals (*e.g.*, Pt, Au, Ag, etc.), regardless of the polarization of the light or its angle of incidence. However, there are some metals (principally the alkalis) for which curves similar to *B* are observed when the light is polarized with the electric vector *E* parallel to the surface, and curves of the type *A* are found whenever there is a component of the electric vector normal to the surface. In still other cases, curves of type *A* are found when there is no component of *E* perpendicular to the surface. We shall discuss for the present only the characteristics of the normal curves obtained with unpolarized light.

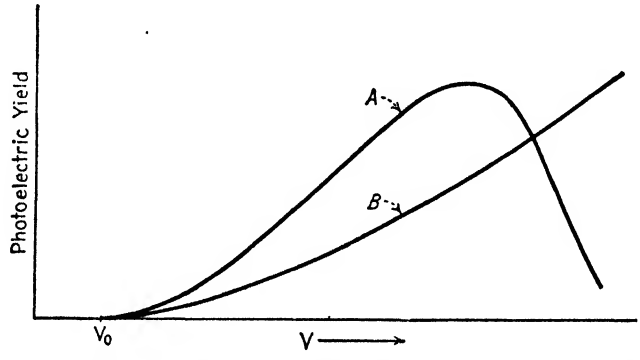

FIG. 4-29.—Types of spectral distribution curves. *A*. Curve showing spectral selectivity. *B*. "normal" curve.

A number of examples of "normal" spectral distribution functions for various metals will be found in the illustrations of Chapter III, and a few of the more careful measurements on clean surfaces are reproduced in Fig. 4-30. The photoelectric yield, referred in each case to unit intensity of incident light, has been plotted as a function of wave-length, although it is probable that frequency, being directly proportional to energy, is of more fundamental significance. The ordinates of the various curves shown are not all plotted to the same scale, and hence the curves can be compared only as to general shape. In only one of these cases has the photoelectric yield been expressed in absolute units, *e.g.*, coulombs per calorie or amperes per watt. It would be highly desirable if the spectral distribution curves for all metals could be given in absolute units, as such data would be of immense practical importance in comparing various metals for use in photoelectric cells for different purposes.

One of the chief points of interest in connection with such curves, and one which has been the subject of some discussion, is the sharpness with which they plunge into the axis at the threshold frequency. This is closely connected, of course, with the question of the existence of a

sharply defined maximum velocity of emission, which has been discussed in the first part of this chapter. The curves may of course approach the axis in one of three different ways: (1) they may show an

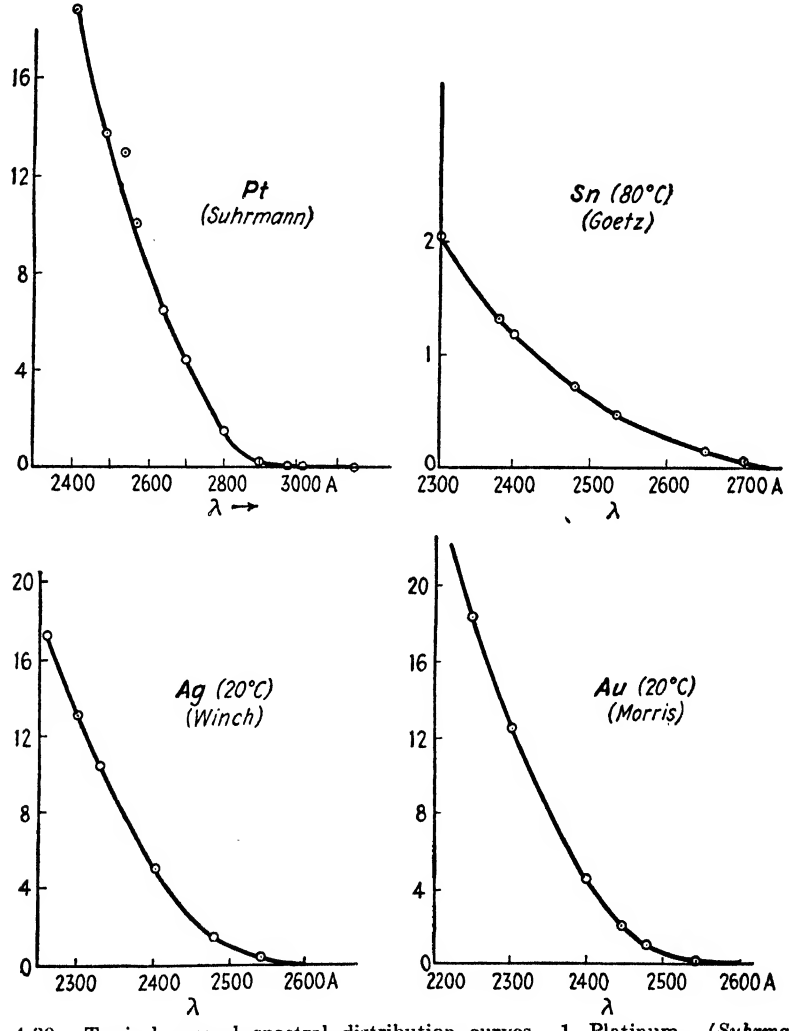

FIG. 4-30.—Typical normal spectral distribution curves. 1. Platinum. (*Suhrmann.*[1]) 2. Tin. (*Goetz.*[2]) 3. Silver. (*Winch.*[3]) 4. Gold. (*Morris.*[4])

asymptotic approach with no definite threshold, (2) they may be tangent to the axis at the threshold, or (3) they may cut the axis at a finite angle (Fig. 4-31). There are cases, of course, in which there are spurious

[1] R. SUHRMANN, *Zeits. f. Phys.*, **33**, 63 (1925).
[2] A. GOETZ, *Phys. Rev.*, **33**, 373 (1929).
[3] R. P. WINCH, *Phys. Rev.*, **37**, 1269 (1931).
[4] L. W. MORRIS, *Phys. Rev.*, **37**, 1263 (1931).

effects—such as the presence of light of short wave-length in the supposedly monochromatic incident beam—which give rise to a pronounced "foot" to the spectral distribution curve and thus give the appearance of an asymptotic approach. These effects have been eliminated in many experiments by the use of pure monochromatic light, and curves are then obtained which can be extrapolated to cut the axis at a finite angle. However, a number of investigations[1] have shown that even when these precautions are taken the curves show a definite tendency to approach the axis at zero angle, if careful measurements are taken

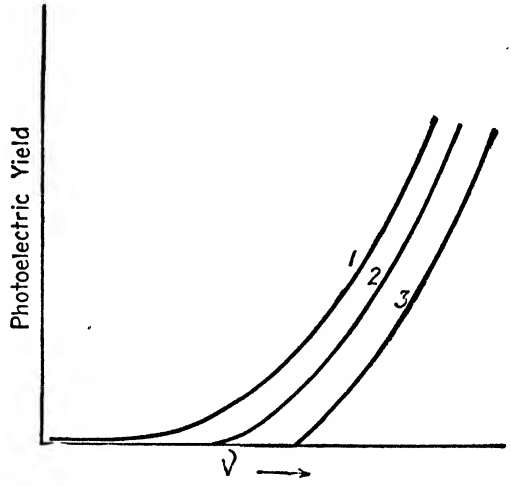

FIG. 4-31.—Showing the three ways in which spectral distribution curves may approach the frequency axis.

in the immediate vicinity of the threshold. This effect is pronounced for contaminated surfaces, as has been shown by Richardson and Young,[2] and also for thin films of the alkali metals. But even for very clean metals the thresholds are probably not sharply defined.[3] As a matter of fact, a sharply defined threshold would scarcely be expected except at absolute zero, because of the thermal energies of the electrons. The tailing off due to this factor may be so small as to be often unobserved experimentally, although as we have seen in the previous chapter, it becomes quite noticeable at higher temperatures. This is in agreement with recent theoretical work of Fowler,[4] from which it appears that the tailing off due to thermal energies makes it impossible to obtain highly accurate values of the threshold by extrapolation of the distribution curves.

[1] R. SUHRMANN, *loc. cit.*, E. O. LAWRENCE and L. B. LINFORD, *Phys. Rev.*, **36**, 482 (1930); H. E. IVES, *Jour. Opt. Soc. Amer.*, **8**, 551 (1924).

[2] O. W. RICHARDSON and A. F. A. YOUNG, *Proc. Roy. Soc.*, **107**, 377 (1925).

[3] R. Suhrmann (*Zeits. f. Phys.*, **33**, 63 [1925]) first recognized this.

[4] Discussed in Sec. **6-30**.

In some cases it is possible to distinguish between an asymptotic approach to the axis and a meeting of the axis at zero tangent by plotting the logarithm of the photoelectric current as a function of wave-length. If the curve actually touched the axis at a definite point the logarithmic curves will approach a vertical tangent at this point. This is seen in the curves obtained by Goetz for tin and by Morris for gold, which have been reproduced in Fig. 3-43, page 107; and Fig. 3-34, page 98. According to Fowler, the spectral distribution curves should be tangent to the axis at the absolute zero but should show an asymptotic approach for all higher temperatures.

4-10. The Presence of Maxima in the "Normal" Spectral Distribution Curves.—While it is usually true that a maximum in the spectral distribution curve can be associated with the selective effect, there is ample evidence that even in the "normal" effect (particularly at normal incidence), the photocurrent sometimes reaches a maximum—usually at frequencies considerably higher than the threshold. For most metals such maxima, if they exist, are too far in the ultra-violet to be observed, but they have been repeatedly observed in the case of the alkali metals, and by Richardson and Compton[1] for aluminum. Several such curves obtained by various observers are to be found in Chapter V. In many cases the maxima occur at a frequency in the neighborhood of $\frac{3}{2}\nu_0$ as predicted by Richardson's theory. The experimental data have not been extended over a sufficiently great range of wave-lengths to bring out any regularities in the appearance of such maxima, and even their existence in many cases may be questioned, due to failure to take account of spurious effects, such as changes in the optical absorption of the surface. It is evident that the distinction between the selective and normal effects here is not sharply defined. For, obviously, if a maximum exists for $E\|$, then it will exist also for unpolarized light when not incident normally, and probably normal incidence can never be attained over a very great portion of any actual surface owing to its irregularities. Thus it is difficult to decide whether or not the presence of a spectral maximum is always due to the presence of $E\|$ light, although at present this view seems the most logical.

4-11. Empirical Equations to Represent Spectral Distribution.—A number of attempts have been made to represent the observed form of the spectral distribution curves by means of empirical equations. Two such equations which seem to fit the experimental data in some cases were suggested by Werner[2] and A. Becker.[3] They are:

$$I = \text{const} \cdot \left(1 - \frac{\lambda}{\lambda_0}\right)^2, \tag{4-5}$$

[1] O. W. Richardson and K. T. Compton, *Phil. Mag.*, **26**, 549 (1913).
[2] S. Werner, *Dissertation, Upsala* (1914).
[3] A. Becker, *Ann. d. Phys.*, **78**, 84 (1925).

and

$$I = \text{const} \cdot \left(1 - \frac{\lambda}{\lambda_0}\right)^3. \tag{4-6}$$

Becker has shown by means of the curves reproduced in Fig. 4-32 that all of the data obtained by Suhrmann and Werner on Pt, Au, and Ag may be represented by one or the other of these functions —and it will be seen that there are but few experimental points which do not fall very close to one of the curves. Whether the points for a given specimen fall upon the cubic or quadratic curve seems to depend in an irregular way upon the condition of the surface.

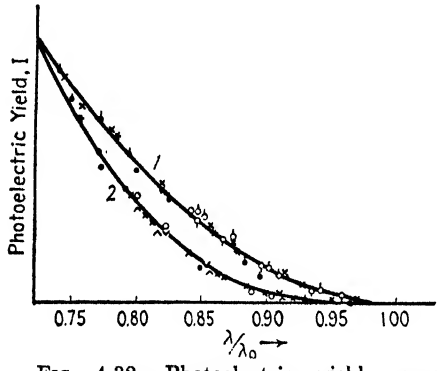

FIG. 4-32.—Photoelectric yield as a function of λ/λ_0. 1. Curve computed from Eq. (4-5). 2. Curve computed from Eq. (4-6). The experimental points represent the data of Suhrmann and Werner on various samples of Au, Ag, and Pt.

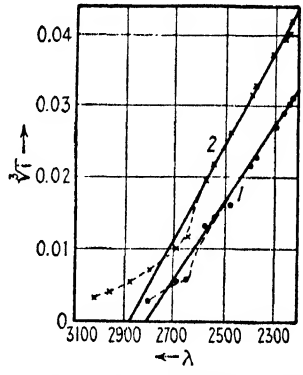

FIG. 4-33.—Experimental test of Eq. (4-6). (*Rumpf.*) Experimental points are data of Suhrmann on Pt (curve 1) and Au (curve 2).

The equations may be more accurately tested by plotting $I^{\frac{1}{2}}$ or $I^{\frac{1}{3}}$ against λ to determine whether the resulting curve is a straight line. This has been done with Suhrmann's data by Rumpf,[1] whose curves are reproduced in Fig. 4-33. He computes the values of the constants in the two equations and finds that they are grouped quite closely about a mean value for the various specimens. There are wide departures from the linear relation for wave-lengths in the vicinity of the threshold, however—as might be expected from the lack of sharpness in the limit found by Suhrmann. The data of Goetz, Kazda, and others, when plotted in this way, show no resemblance to a linear relation, proving that these equations are not of general validity.

Several equations for the spectral distribution function have been derived on the basis of various theories of the photoelectric process, and these will be discussed in Chapter VI.

[1] E. RUMPF, *Zeits. f. Phys.*, **37**, 165 (1926).

CHAPTER V

THE SELECTIVE PHOTOELECTRIC EFFECT

A discovery by Elster and Geitel, many years ago, opened up one of the most interesting and puzzling fields in photoelectricity.[1] They found that the photoelectric current from the surface of sodium-potassium alloy (a liquid) depended to an extraordinary extent upon the plane of polarization of the light. Thus when the beam (incident at 60 deg) was polarized so that the electric vibrations were parallel to the plane of incidence, the photoelectric current was as much as sixty times that obtained when the beam was polarized so that the electric vibrations were perpendicular to this plane (and so were parallel to the surface). This effect received a plausible qualitative interpretation on the electromagnetic theory of light, for it was natural to assume that the electrons could escape more easily when the electric vector had a component perpendicular to the surface than when it was entirely parallel to the surface. But the quantum theory, so successful in some aspects of photoelectricity, could give no indication of an explanation until quite recently, when Fowler[2] applied the conceptions of wave mechanics to the problem.

5-1. Optical Considerations and Terminology.—We shall denote the two principal planes of polarization of a beam of light obliquely incident on a surface as the $E\|$ and the $E\perp$ plane. In the $E\|$ case, the electric vector vibrates parallel to the plane of incidence; while in the $E\perp$ case, it vibrates perpendicularly to the plane of incidence. "$E\|$ light," "the $E\|$ case," etc., are convenient self-explanatory abbreviations. Where necessary, we shall use $I\|$ and $I\perp$ to denote the corresponding photoelectric currents, and $L\|$ and $L\perp$ to denote the energies associated with the corresponding polarized beams.

The next step was taken by Pohl, who investigated the effect for highly reflecting mirrors of Pt and Cu (sputtered on to quartz) and Hg.[3] Typical results are given in Fig. 5-1. On calculating the different amounts of light energy absorbed by means of Drude's formulas

$$L\perp = \frac{4n\cos\psi}{n^2(1+k^2)+2n\cos\psi+\cos^2\psi},$$
$$L\| = \frac{4n\cos\psi}{n^2(1+k^2)\cos^2\psi+2n\cos\psi+1}, \tag{5-1}$$

[1] J. Elster and H. Geitel, *Ann. d. Phys.*, **52**, 433 (1894); **55**, 684 (1895); **61**, 445 (1895).

[2] R. H. Fowler, *Proc. Roy. Soc.*, **128**, 123 (1930).

[3] R. Pohl, *Verh. d. Deutsch. Phys. Ges.*, **10**, 339, 609, 715 (1909).

where n is the refractive index, k the absorption index, and ψ the angle of incidence, he showed that $I\|/I\perp$ was equal to $L\|/L\perp$ for all angles of incidence. Hence the differences in the photoelectric currents are completely accounted for by differences in the amount of light absorbed. But for a highly reflecting surface of Na-K alloy, Pohl and Pringsheim[1] obtained, in agreement with the earlier work of Elster and Geitel, a ratio $I\|/I\perp$, far too high to be accounted for by any reasonable assumptions as to the values of the optical constants. They also found that, for Na-K alloy, $I\|$ and $I\perp$ changed with the wave-length of the light in the way shown in Fig. 5-2. They denoted a yield increasing steadily towards shorter wave-lengths as a *normal effect* (*e.g.*, $I\perp$ in Fig. 5-2), while a resonance-like curve (*e.g.*, $I\|$ in Fig. 5-2) was supposed to indicate the presence of a *selective effect*. Assuming that the experimental curve $ABGD$, for $E\|$ light, is composed of a selective part superposed on a nor-

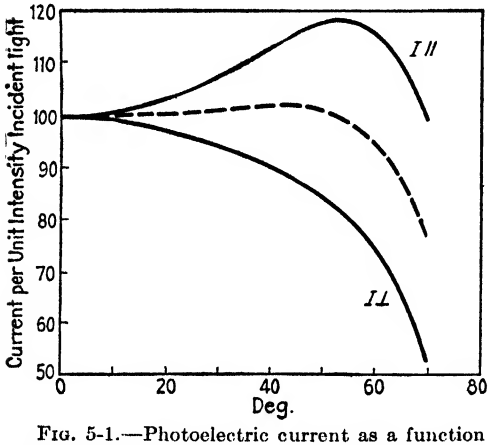

FIG. 5-1.—Photoelectric current as a function of the angle of incidence. Unresolved ultra-violet light. Unbroken line, current for polarized light. Broken line, current for unpolarized light.

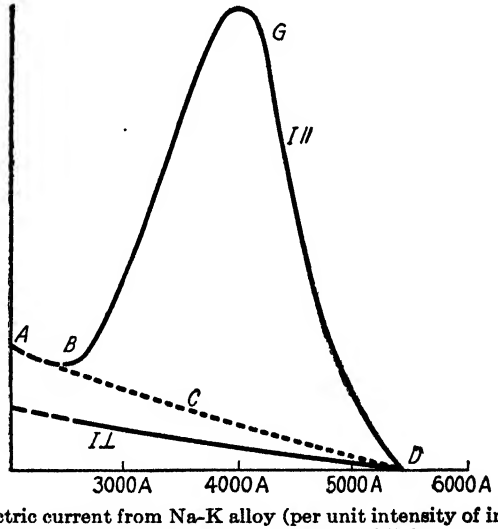

FIG. 5-2.—Photoelectric current from Na-K alloy (per unit intensity of incident light) when illuminated obliquely by polarized light.

[1] R. POHL and P. PRINGSHEIM, *Verh. d. Deutsch. Phys. Ges.*, **12**, 682 (1910).

mal curve *ABCD*, it is possible to construct a set of selective curves showing how they depend on the angle of incidence (Fig. 5-3).

We shall now introduce two new terms to describe two distinct effects which happen to be associated together in the results described in the previous paragraph. There is, however, no *a priori* reason for believing that they must occur together.

1. *Polarization selectivity* is present when the ratio $I\|/I\perp$ exceeds the ratio $L\|/L\perp$, or, alternatively, when it is impossible to account for the difference in the photoelectric current as we substitute $E\|$ light for $E\perp$ light merely by a change in the amount of light absorbed. (As we

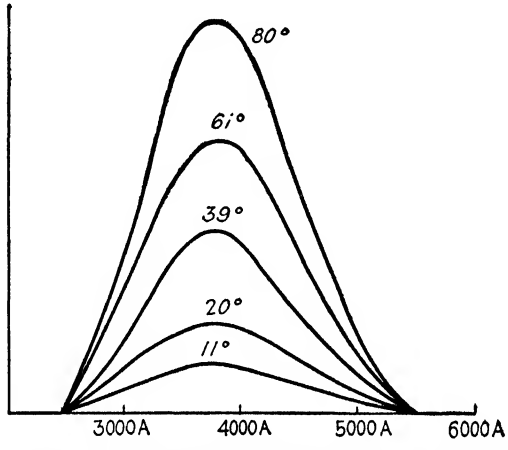

FIG. 5-3.—Selective effect for Na-K alloy at different angles of incidence (referred to unit energy of incident light).

approach zero angle of incidence, the distinction between $E\|$ and $E\perp$ disappears; hence we find that, as a rule, experiments on polarization selectivity are carried out with angles of incidence between about 40 and 80 deg.)

2. *Spectral selectivity* is present when there is a maximum in the photoelectric yield when plotted as a function of λ. This maximum may occur in the $E\|$ curve alone, or in both the $E\|$ and the $E\perp$ curves.

The conditions under which the majority of the investigations have been carried out are such as to make it unnecessary and perhaps even undesirable, at any rate at the present time, to make these definitions more precise and therefore more limited.

The optical constants are unknown for most metallic surfaces; hence we cannot compute $L\|/L\perp$. For such surfaces the best we can do is (following Ives) to consider a ratio of $I\|/I\perp$ exceeding 3 or 4 for angles of incidence between 40 and 80 deg to indicate the presence of polarization selectivity, merely because a value exceeding 3 or 4 for $L\|/L\perp$ has never been found for surfaces whose optical constants are known.[1]

[1] A good list of optical constants will be found in the "International Critical Tables," Vol. V, p. 248 (McGraw-Hill Book Company, Inc., 1929).

In the absence of polarization selectivity, since $I\| = k \cdot L\|$ and $I\perp = k \cdot L\perp$ where the k's are identical, the graphs representing the L's as a function of the angle of incidence also represent the I's. If, however, there is polarization selectivity, then the k in the $E\|$ case is much larger than in the $E\perp$ case, and indeed is not a constant. Elster and Geitel found that, by suitably dividing $I\|$ into two parts ($I\|[1]$ and $I\|[2]$) and associating the first part with the component of the $E\|$ vector which is perpendicular to the *surface* of the metal, $L\|[1]$, and the second part with the component parallel to the surface, $L\|[2]$, then $I\|[1] = k_1 \cdot L\|[1]$ and $I\|[2] = k \cdot L\|[2]$, where k_1 is now a constant much larger than k. This significant result stands alone; no reexamination of these relations appears to have been made in the last 30 years. At normal incidence, $E\|$ and $E\perp$ become indistinguishable and must necessarily give rise to identical photoelectric currents, while at 90 deg. (glancing incidence) there is no absorption (Eq. [5-1]), and therefore no photoelectric current.

It is found experimentally that, whenever there is a sharp maximum in the spectral distribution curve for unresolved light, it is due, almost always, to the $E\|$ component. (If the surface, for which the curves in Fig. 5-2 were obtained, had been illuminated by unresolved light, the resulting curve, because it is the sum of the $I\|$ and $I\perp$ curves, would show a sharp maximum.) Then if $I\|/I\perp$ were plotted against λ, there would also be a maximum in this curve. This may or may not imply polarization selectivity; we cannot tell unless the ratio $L\|/L\perp$ is measured and compared with $I\|/I\perp$. When $L\|/L\perp$ is not measured, we consider as a rough criterion for the presence of polarization selectivity a value in excess of 3 or 4 for $I\|/I\perp$.

✓ It has been found recently that a maximum in the spectral distribution curve, obtained by plotting the photoelectric current per unit energy of *incident light*, is sometimes due to a selective absorption by the surface. In such cases the maximum disappears when the current is measured per unit energy of *absorbed light*. We should not, of course, call this a spectral selectivity, but, inasmuch as very few investigators have referred their currents to absorbed light, we prefer, for the present, to let the term spectral selectivity cover all cases where the spectral distribution curve passes through a maximum in the visible or near ultra-violet region.

In all measurements on spectral selectivity it is necessary to have a measure of the intensity of the light used. This is generally obtained by placing a suitable thermopile at the exit slit of the monochromator. Alternatively one may use a white light source and, knowing its color temperature, it is possible to compute the energy in any part of the spectrum. In this case, due allowance must be made for the variation in the dispersion and absorption of the monochromator along the spectrum. The amount of energy available in the ultra-violet radiation from most

sources is generally so small as to tax the sensitivity of the thermopile and its associated galvanometer to the utmost. With a white light source it is not necessary to make actual energy measurements, but unfortunately the available energy falls off steeply towards shorter wave-lengths and is very small in the ultra-violet.

The first step in a quantitative study of the photoelectric yield is to measure the amount of light energy incident on the photoelectric surface. But it is evident that a closer approximation to the quantities which are fundamentally important is secured when we go further, and relate the photoelectric current to the amount of light *actually absorbed* in the surface. A still further refinement would call for an exact knowledge of the depths of penetration of the light, for it is evident that the number of photoelectrons escaping from a surface is larger the more quickly the light is absorbed, other things being equal. So far as we know, no attempt has been made to allow for this factor; we merely draw attention to the desirability of including it in a really complete description of a photoelectric effect, although it is recognized that, at the present stage of development, it is not expedient to attempt to go beyond a measurement of the amount of energy absorbed by the surface.

Knowing the energy of light incident upon a surface, it is possible to calculate the amount absorbed by the surface by means of Equations (5-1) derived by Drude on the electromagnetic theory. The optical constants necessary for the application of these formulas have been determined in a few cases by Minor and Voigt and others.[1] The fact that these constants were not determined for the metal surfaces actually used in photoelectric experiments is always a possible explanation of discordant results. It would, of course, be better to determine the energy absorbed by measuring the difference between the incident energy and the reflected energy. But in the case of a highly reflecting surface, it is a matter of some difficulty to measure accurately the relatively very small difference between the incident and reflected energies. It has, however, been done successfully by Fleischer and Dember.[2]

An ingenious method of utilizing the whole of the incident energy so that it is also a measure of the absorbed energy is that of Pohl and Pringsheim.[3] If the active material is spread over the whole of the inside of a hollow sphere, except for a small window through which to admit the light, then a suitably directed beam (Fig. 5-4, ray 2) will be reflected to and fro inside the sphere until it is completely absorbed. (The diagram shows the case of an optically reflecting surface; the trapping of the light would be equally good for a matte surface.) Thus when

[1] A good list of optical constants will be found in the "International Critical Tables," Vol. V, p. 248 (McGraw-Hill Book Company, Inc., 1929).

[2] R. Fleischer and H. Dember, *Zeits. f. Tech. Phys.*, **7**, 137 (1926).

[3] R. Pohl and P. Pringsheim, *Verh. d. Deutsch. Phys. Ges.*, **15**, 111 (1913).

the spherical surface is the cathode and the beam is directed along 2, the photoelectric current is given in terms of the absorbed energy. If the plate P is the cathode, and the beam is directed along 1, the photoelectric current is given in terms of the incident energy. Thus it is possible in one and the same cell to refer the photoelectric current either to incident energy or to absorbed energy.

The above method has been used only for unpolarized light and without regard to the angle of incidence. In principle it would be possible to measure the photoelectric current per unit energy of absorbed light (polarized either in the $E\|$ or the $E\perp$ plane), at a known angle of incidence, by making a cylindrical cell whose section is like that of Fig. 5-4. Provided that the inside surface is an optically reflecting cylinder, a ribbon of light entering along ray 2 would always maintain the same angle of incidence at successive reflections and the same state of polarization.

5-2. Polarization Selectivity: Alkali Metals (Thick Layers).—Pohl and Pringsheim[1] found that the polarization selectivity ratio in Na-K

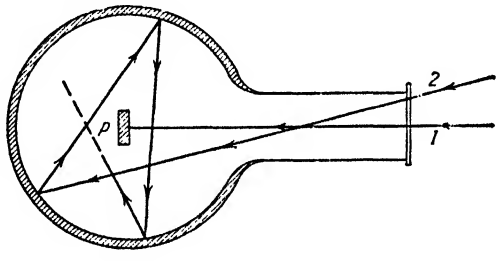

FIG. 5-4.

alloy varied in a capricious manner from cell to cell, although the position of the maximum in the spectral selectivity curve remained practically constant. Thus with one cell they obtained a ratio of 300:1 for $I\|/I\perp$ at the spectral selectivity maximum, while frequently for other cells ratios between 10:1 and 20:1 were obtained (60-deg incidence). Referring to Fig. 5-2, this means that the peak of the $E\|$ curve, while remaining almost unchanged as to position, may in some cells be highly accentuated while in others it may be of moderate height. They were unable to find the conditions which controlled the ratio $I\|/I\perp$. Ives, Olpin, and Johnsrud[2] mention that merely pouring the alloy from one part of an exhausted experimental tube to another part, where it was conceivable that the vacuum was not quite so good, increased the ratio very considerably.

It might be expected that, for normal incidence, a curve similar to the $E\perp$ curve for oblique incidence might be obtained, since in both cases the electric vector has no component perpendicular to the surface.

[1] R. POHL and P. PRINGSHEIM, *Verh. d. Deutsch. Phys. Ges.*, **12**, 1039 (1910).
[2] H. E. IVES, A. R. OLPIN, and A. L. JOHNSRUD, *Phys. Rev.*, **32**, 57 (1928).

This was found to be the case by Hallwachs[1] who found that the spectral distribution curve fitted Becker's empirical equation,

$$f(\lambda) = \text{const} \cdot \left(1 - \frac{\lambda}{\lambda_0}\right)^2$$

a function which has no maximum.

Farwig[2] made some careful measurements on the $I\|/I\perp$ ratios for Na-K alloy and for K held just above the melting point. His curves (*e.g.*, Fig. 5-5) indicate that the selective effect is to be regarded as an effect superposed on a normal effect near the threshold, but certainly not at it, as had hitherto been believed.

All results hitherto discussed were obtained with alloys in which the sodium and potassium were in approximately equal atomic proportions.

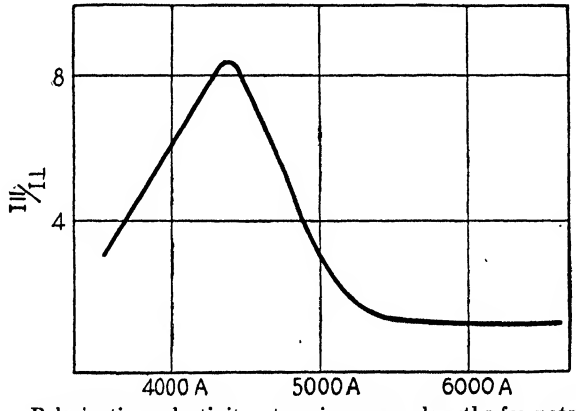

FIG. 5-5.—Polarization selectivity at various wave-lengths for potassium.

Ives and Stilwell[3] studied systematically the effect of varying the proportions of the constituent metals. Their results are shown in Fig. 5-6. It is evident that the composition of the alloy has a profound influence on the value of the ratio $I\|/I\perp$. We see that alloys with 20 and 90 per cent sodium in them give high ratios, as well as the hitherto investigated 50 per cent alloy. This ratio, $I\|/I\perp$, was always less for completely melted alloys than for semimolten alloys, which is to be expected on the working hypothesis that the degree of orientation of atoms in the surface is probably closely related to the magnitude of the ratio $I\|/I\perp$. By means of a special type of cell, in which the proportions of sodium and potassium could be varied by small steps, these authors measured $I\|$ and $I\perp$ separately (Fig. 5-7). It is evident that both curves contribute to the change in the ratio $I\|/I\perp$ in a complicated manner.

[1] W. HALLWACHS, *Ann. d. Phys.*, **30**, 593 (1909.)
[2] K. FARWIG, *Zeits. f. Phys.* **21**, 38 (1923).
[3] H. E. IVES and G. R. STILWELL, *Phys. Rev.*, **29**, 252 (1927).

Ives and Johnsrud[1] obtained the results shown in Figs. 5-8 and 5-9 for the five alkali metals and their alloys, all being in the liquid state. (The composition of the alloys was not determined; it was such as to give the lowest melting point.) The remarkable result of this systematic investigation is that the very high $I\|/I\perp$ ratios are obtained only with the Na-K alloy. The ratios for all the others, while probably too large to be accounted for by possible values of $L\|/L\perp$, were between about 3:1 and 5:1. Most of the metals, however, show *spectral* selectivity, which in Rb is to be found even for $E\perp$, as well as for $E\|$. It is possible, however, as the authors point out, that the $I\|/I\perp$ ratios may be

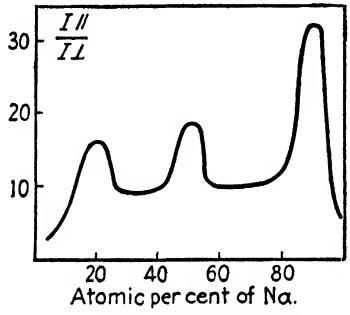

FIG. 5-6.—Polarization selectivity of various Na-K alloys all at temperatures above their melting points.

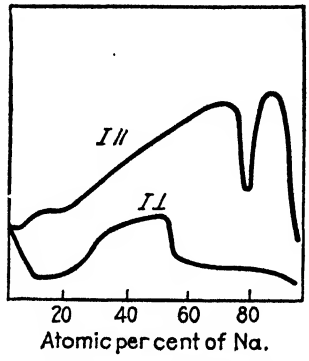

FIG. 5-7.—Polarization selectivity of various Na-K alloys; $I\|$ and $I\perp$ measured separately. The scale for $I\|$ is smaller than that for $I\perp$.

profoundly altered by varying the composition of the alloys as in the case of the Na-K alloy.

Convincing evidence that strong polarization selectivity and spectral selectivity are due to some kind of an absorbed film was found by Fleischer.[2] He outgassed his potassium with extreme care. On illuminating the mirror-like surface with polarized light, he obtained no indication of either type of selectivity (Fig. 5-10). But when he released a little hydrogen (which did not visibly affect the potassium) by heating a hydrogen-charged platinum wire in the cell, he obtained strong selectivity as shown in the diagram. The spectral selectivity has a maximum at 4360A. A similar experiment with oxygen brought out a weak spectral selectivity maximum at 3130A.[3,4] These experiments are important

[1] H. E. IVES and A. L. JOHNSRUD, *Astrophys. Jour.*, **60**, 232 (1924).

[2] R. FLEISCHER, *Ann. d. Phys.*, **82**, 75 (1927).

[3] R. FLEISCHER, *Ann. d. Phys.*, **82**, 243 (1927).

[4] Note: An examination of Fleischer's curves indicates that (1) before true spectral selectivity appears, and (2) after it appears, but in the region outside it, the ratio $I\|/L\|$ is of the order of 50 to 100 per cent greater than the ratio $I\perp/L\perp$. Hence, in

because they show that spectral selectivity may, in some cases, be completely accounted for by selective absorption. True spectral selectivity is that which persists even after absorption has been taken into account, but in the present state of the subject it is not expedient to restrict the term so closely.[1]

Ives and Johnsrud[2] found that the increase in the polarization selectivity of sodium-potassium alloy, as it cooled down from a temperature at which noticeable distillation began, was due entirely to a diminution in the $I\perp$ current, the $I\|$ current remaining constant throughout. (The ratio $I\|/I\perp$ increased from 2:1 to 15:1.) Wolf,[3] however, found that the $I\|$ current diminished more rapidly than the $I\perp$ current, as time went on, the cell in his experiments being presumably kept at room temperature.

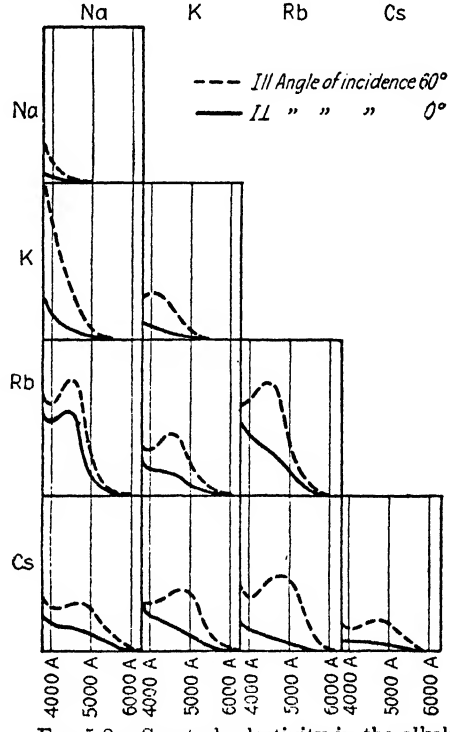

FIG. 5-8.—Spectral selectivity in the alkali metals and their alloys. Broken line, $I\|$; angle of incidence 60°. Unbroken line, $I\perp$; angle of incidence 0°. (Current per unit incident energy.)

5-3. Polarization Selectivity: Alkali Metals (Thin Films).—Our knowledge of the peculiar photoelectric properties of thin films began with an observation by Geitel[4] in 1922. He noticed that, in a cell containing a potassium cathode, the anode, although not visibly coated with potassium, was photoelectrically sensitive. Heating the anode drove off the active substance, but in a few minutes after cooling the photoelectric sensitivity returned. Evidently a thin film of potassium had condensed on the anode and made it photoelectrically sensitive.

We shall define a thin film for the purposes of this chapter as that film which forms spontaneously, at room temperature, on all surfaces in

a sense, polarization selectivity occurs here without spectral selectivity. Too much attention, however, should not be paid to this interpretation, as Fleischer himself makes no comment on it and his units may differ in the two sets of curves.

[1] Ives (*Phys. Rev.*, **38**, 1920 [1931]) has recently obtained evidence which points strongly to the conclusion that polarization selectivity is *entirely* an optical phenomenon and this might be true of *spectral* selectivity also.

[2] H. E. Ives and A. L. Johnsrud, *Astrophys. Jour.* **60**, 232 (1924).

[3] F. Wolf, *Ann. d. Phys.*, **83**, 1001 (1927).

[4] H. Geitel, *Ann. d. Phys.*, **67**, 420 (1922).

a cell containing an alkali metal. It is quite invisible and difficult to detect by any test except by its photoelectric sensitivity. Investigators have frequently found it convenient to employ cathodes formed by the evaporation of an alkali metal on to a suitably shaped metal plate until the plate is visibly covered by the alkali metal. It is to be emphasized

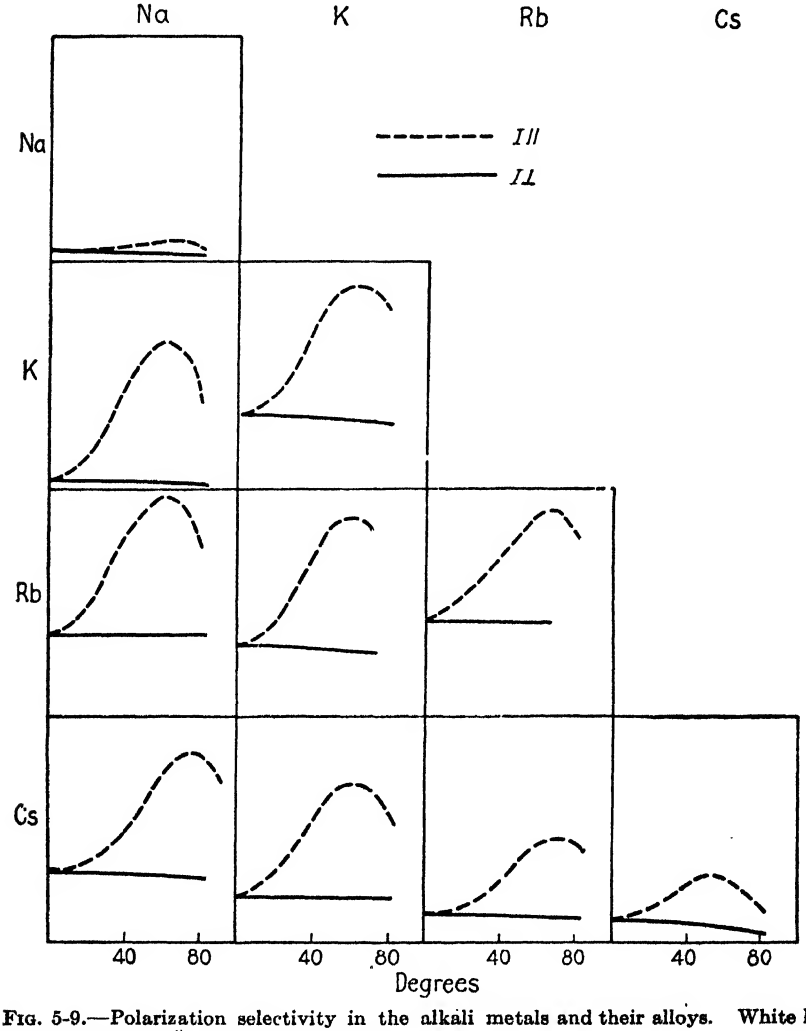

FIG. 5-9.—Polarization selectivity in the alkali metals and their alloys. White light used. Broken line, $I\|$. Unbroken line, $I\perp$.

that such a deposit is not technically a *thin film;* we shall use the term *thick layer* for such a deposit, as well as for the alkali metal in bulk, because it is many atoms thick. We follow Ives in calling the film, which forms on a metal or glass surface in a vacuum cell containing an alkali metal, after enough time has elapsed to allow it to reach its equilibrium

thickness at ordinary temperatures, the "spontaneously deposited film." Almost all the interesting variations in the photoelectric properties of thin films occur as the film is made *thinner* than this equilibrium value by controlled heating. There are reasons for believing that the spontaneously deposited film consists of two or three layers of closely packed atoms.

Ives[1] was the first to obtain data on the polarization selectivity of spontaneously deposited films of potassium. The supporting metals

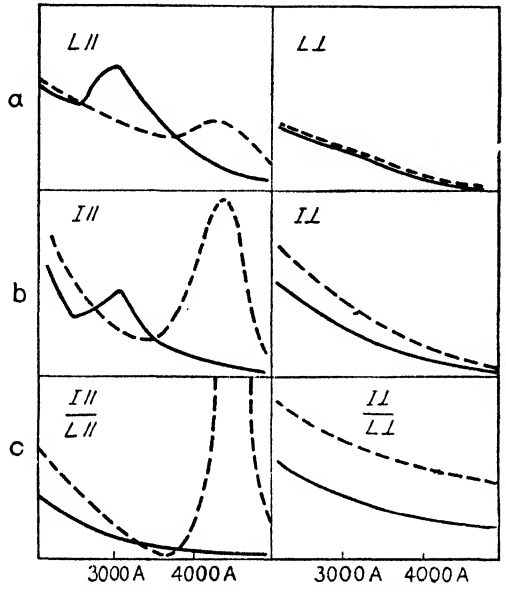

FIG. 5-10.—Spectral and polarization selectivity in potassium. Unbroken line, outgassed K, broken line, K exposed to H_2: angle of incidence = 45°. *a*. Optical absorption. *b*. Photoelectric current per unit *incident* light. *c*. Photoelectric current per unit *absorbed* light.

used were Au, Cu, Ag, Pt, Ni, W, Ta, and C. The $I\|$ and $I\perp$ curves varied with the angle of incidence much in the same way as was shown in Fig. 5-1, except that in many cases the $I\|/I\perp$ ratio was considerably higher. His curves are summarized in Table 5-1. It is evident that some thin films show marked polarization selectivity. No definite correlation with the properties of the supporting metal could be traced, except that the $I\perp$ currents apparently increased with the reflecting power of the underlying metal. The $I\|/I\perp$ ratio was five times greater for a thin film of K on Pt than for a thick layer of K, while the $I\perp$ currents in each case were about equal. Within the range 6000A to 3800A, Ives found no indication of spectral selectivity, and consequently, if any exists, it must be farther in the ultra-violet.

[1] H. E. IVES, *Astrophys. Jour.*, 60, 209 (1924).

The thickness of the film can be controlled in two ways. The cell can be immersed in liquid air and the film made to disappear gradually by suitably heating the internal cathode on which it is supported. Alternatively, the cell can be maintained at room temperature and the central cathode made film free by heating. As it cools, the film builds up again. The equilibrium thickness of the spontaneously deposited

TABLE 5-1.—POLARIZATION SELECTIVITY OF THIN FILMS OF POTASSIUM

Supporting metal	Currents at 70 deg incidence (relative values)				Polarization selectivity at 70 deg	
	Blue light		Yellow light		Blue light	Yellow light
	$I\parallel$	$I\perp$	$I\parallel$	$I\perp$	$I\parallel/I\perp$	$I\parallel/I\perp$
Au	12	5	8	4	2.4	2.0
Cu	68	10	11	2	6.8	5.5
Ag	67	12	6	1.5	5.6	4.0
Pt	98	4	4	1.5	24.6	4.7
C	9.5	1.5	3	1	6.3	3.0
W	54	5	7	1	11.0	7.0
Ni	66	6	17	2	11.0	8.5
Ta	98	4	14	1.5	24.6	9.5

Ratios refer to incident light, not to absorbed light.

film is attained after several hours with Na, after several minutes with K, and after several seconds with Rb and Cs. Consequently it is easiest to study the photoelectric properties of a forming film in the case of Na. In the case of other metals, Ives found it more convenient to follow the properties of a film as it is made thinner by heating. He found that the photoelectric properties of a thin film depend on the thickness alone; it is immaterial whether the film is forming or breaking up. Both the $I\parallel$ and the $I\perp$ currents from a forming film of Na, as well as the $I\parallel/I\perp$ ratio, attain their maximum values long before the film attains the equilibrium thickness of a spontaneously deposited film (Fig. 5-11). The maximum in the ratio occurs at a considerably later stage in the formation of the film than the maximum in the individual currents. Ives states that in the earliest stages of the formation of a film, $I\parallel/I\perp$

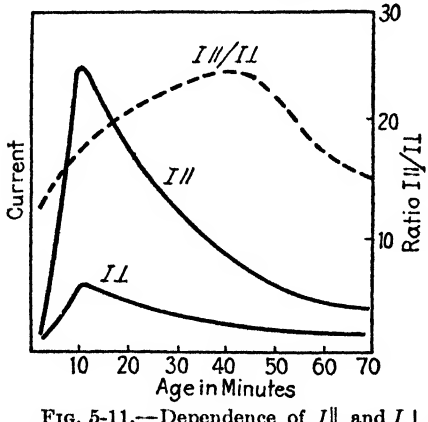

FIG. 5-11.—Dependence of $I\parallel$ and $I\perp$ on age of film. $I\parallel$ for 80° incidence. $I\perp$ for 0° incidence. $I\parallel/I\perp$, *both* for 80° incidence.

does not exceed 2 or 3. In a later note, Ives and Briggs[1] state that they find that the ratio $I\|/I\perp$ drops to 1 for films thinner than had been investigated in the previous work, while in the case of exceedingly thin films the ratio actually becomes less than 1.

The increase in the ratio $I\|/I\perp$ is due mainly to a decrease in $I\perp$, a result analogous to that obtained by Ives for thick layers and discussed in the previous section.

Films of rubidium spontaneously deposited on glass are photoelectrically active and conduct electricity according to Ohm's law.[2] A polarization selectivity of about 5:1 was observed with white light, incident at 70 deg. While not strictly comparable with the results previously discussed for films on metals, there is no indication of outstanding differences between the properties of a film on glass and those of one on a metal. The photoelectric current was about 2.5 times that from a Rb film on Pt.

By extending the range of wave-lengths employed to 3000A, Suhrmann and Theissing[3] were able to show that there was a close association between polarization selectivity and spectral selectivity for a thin film of potassium on platinum. The cathode employed was a plane mirror of platinum, on to which had been evaporated a trace of potassium from a side tube. The thickness of the film was diminished in steps by electronic bombardment of the platinum on the rear side. The adjacent parts of the experimental tube were suitably cooled to avoid reevaporation of the potassium. The results obtained are assembled in Fig. 5-12. Where comparison is possible, these results are in accord with those of Ives. A high photoelectric yield is evident for the thinnest film; the maximum polarization selectivity does not show itself until a later stage.[4] It is evident that the polarization selectivity and the spectral selectivity have maxima at about the same wave-length.

The researches of Ives and of Suhrmann and Theissing both indicate that the maximum yield and polarization selectivity are obtained with very thin films and that, as one goes over to thick layers, the yield and polarization selectivity fall very considerably. But in view of the profound effect of minute traces of gas on thick layers of potassium, as discussed in the previous section, it would be interesting to study the photoelectric

[1] H. E. Ives and H. B. Briggs, *Phys. Rev.*, **35**, 669 (1930).

[2] H. E. Ives and A. L. Johnsrud, *Astrophys. Jour.*, **62**, 309 (1925).

[3] R. Suhrmann and H. Theissing, *Zeits. f. Phys.*, **55**, 707 (1929).

[4] Note: (1) the maxima in the $I\|$ and $I\perp$ curves, (2) the maximum in the $I\|/I\perp$ ratio, and (3) the maximum shift in the threshold to the red (as we shall see in Sec. **5-12**, p. 178) all occur for thicknesses less than that of the "spontaneously deposited film." Dr. J. A. Becker has kindly informed us that the available evidence points to the conclusion that the spontaneously deposited film is probably two to three atomic layers thick, while a single atomic layer is sufficient to give rise to the maximum photoelectric current.

effects of thin films thoroughly outgassed, and then deliberately exposed to gases. Although a large amount of work has been done recently on adsorbing thin films of gases between the alkali-metal film and the supporting metal (mainly with a view to increasing the yield of photoelectric cells), none of the work has been done with polarized light.

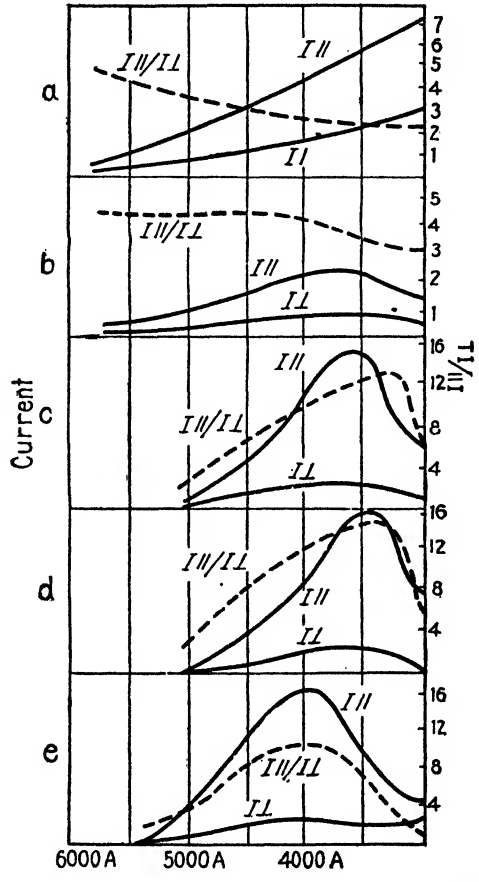

FIG. 5-12.—Selectivity of K films at various thicknesses:

	$I\parallel$ at max.	Max. of $I\parallel/I\perp$
a extremely thin	10×10^{-3} coul/cal	
b very thin	10×10^{-3}	
c thin	40×10^{-3}	13
d thicker	56×10^{-3}	14
e thicker (just visible)	4×10^{-3}	9.7

Yield in terms of incident energy.

5-4. Alkali-metal Thin Films. Sundry Properties.—The thickness of a rubidium film spontaneously deposited on glass in a vacuum was successfully measured by Ives and Johnsrud.[1] They directed a beam of light, polarized at an azimuth of 45 deg. on to a glass plate, and examined

[1] H. E. IVES and A. L. JOHNSRUD, *Jour. Opt. Soc. Amer.*, **15**, 374 (1927).

the reflected light by means of a Babinet compensator and a Nicol prism to determine the shift in phase as a rubidium film formed on the glass. The results indicated that the equilibrium thickness of the spontaneously deposited film was about 6×10^{-8} cm, which is close to the accepted diameter of the Rb atom, *viz.*, 4.5×10^{-8} cm. Consequently we may infer that the thin film is one atom thick. A subsidiary experiment showed that the same film gave the full photoelectric emission of rubidium in bulk. These authors call attention to the fact that the optical theory on which the change of phase of the reflected beam is determined by the thickness of the film implicitly assumes the media involved to be continuous and, consequently, this has to be borne in mind when the calculations lead to a thickness of atomic dimensions.

A possible way of securing films of known thickness would be to arrange to have a "molecular gun" directing a beam of alkali-metal atoms from a chamber containing metal vapor at a known pressure, on to a suitable metal plate cooled by liquid air so as to insure that every atom striking it is immediately frozen on to the surface. The number of atoms striking the plate per second could be calculated from the vapor pressure and the geometry of the molecular gun.[1] It is not self-evident that the polarization selectivity of thin films produced in this way would be necessarily the same as that of the films already studied. A possible difference between the character of the films produced this way and that of those produced in Ives' and Suhrmann's experiments is suggested by Wood's old experiments[2] on the nature of Zn and Cd films deposited on glass in a vacuum. It will be remembered that he found that, when the receiving surface was cooled below about $-100°C$, each atom stayed exactly where it struck the surface, while if the temperature were higher the atoms collected in tiny groups isolated by clear spaces. Such an effect is likely to occur with alkali metals, on glass surfaces if not on others.

The photoelectric current from a thin film of potassium on a tungsten plate is almost saturated at zero voltage when the film has attained the equilibrium thickness of a spontaneously deposited film. But if the film is reduced very considerably in thickness by evaporation (*e.g.*, to the stage where the ratio $I\|/I\perp$ is not more than about 2:1), it is found that an accelerating voltage of 50 volts or so is required to produce saturation.[3] This is satisfactorily explained by Becker's "ion-grid" theory,[4] which was developed to account for an analogous phenomenon

[1] In a very recent note Brady (*Phys. Rev.*, **37**, 230 [1931]) states that, on carrying out an experiment of this kind, he finds that the maximum emission occurs when the thickness of the K is about five atomic layers, and that a film, twelve atomic layers or more thick, has the characteristics of K in bulk.

[2] R. W. Wood, *Phil. Mag.*, **32**, 364 (1916); see also J. D. Cockcroft, *Proc. Roy. Soc.*, **119**, 293 (1928).

[3] H. E. Ives, *Astrophys. Jour.*, **60**, 209 (1924).

[4] J. A. Becker, *Phys. Rev.*, **31**, 431 (1928); **35**, 1431 (1930).

in thermionics. When only a small fraction of the surface of a clean W or Pt plate is covered by Cs, Rb, or K atoms, the atoms are all ionized (Fig. 5-13). If we regard the metal ions as analogous to the grid in a three-electrode radio tube, it is easy to see that the field between the ion grid and the supporting metal helps the electrons out of the latter. Before they can all be drawn away from the surface, the applied field must be strong enough to overcome the local fields; hence, the poor saturation observed.

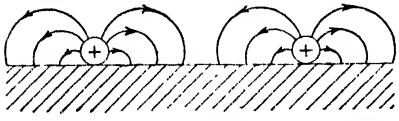

FIG. 5-13.—Schematic representation of a W surface partially covered by Cs^+ ions.

Ives investigated simultaneously the thermionic current and the photoelectric emission from a caesium-coated platinum filament.[1] As the temperature was increased to 650°K, the photoelectric current increased very slowly, but between 650 and 750°K it increased rapidly to a maximum of four times its original value, dropping to zero at about 1000°K. The thermionic current obtained from the same filament is also shown in Fig. 5-14. Evidently the maximum photoelectric current is obtained when a considerable portion of the Cs is driven off, leaving a sufficient number of Cs^+ ions on the surface to allow the ion-grid effect to reach its maximum. It is probable, though not actually tested in this experiment, that the shift of the threshold towards the red is greatest for the film which remains on at about 750°. This is also the condition for a minimum work function, which accounts for the large thermionic emission at so low a temperature. At temperatures above 1000°K the Cs is driven off the surface and its characteristics are now those of clean platinum.

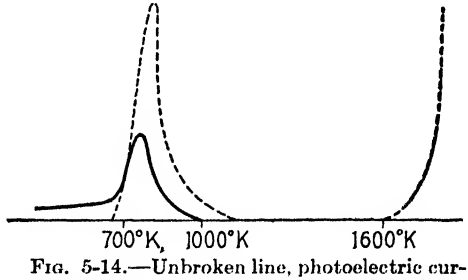

FIG. 5-14.—Unbroken line, photoelectric current from Cs on Pt. Broken line, thermionic current from Cs on Pt.

It is interesting here to call attention to a remarkable difference between the dependence of the photoelectric current on film thickness in the case of alkali-metal films and that in the case of films of platinum or silver deposited on quartz or glass (Stuhlmann, Compton and Ross, Dember and Goldschmidt; Sec. **14-1**, page 494). In the first case the maximum current is obtained when single alkali-metal atoms are distributed here and there over the surface; in the second case a film thickness of the order of 30 atomic diameters is necessary to give the maximum current. The view that atoms may be adsorbed as ions on surfaces when the work function of the surface is greater than the ionization potential of the

[1] H. E. IVES, *Astrophys. Jour.*, **64**, 128 (1926).

adsorbed ion has been used with success by Langmuir and Kingdon,[1] and by Becker.[2] This condition is satisfied by most alkali metals on the usual supporting metals, and perhaps also on glass. On Becker's ion-grid view the main function of the occasional adsorbed ion is to diminish the work function of the composite surface and, so to speak, to let out the electrons from the supporting material. But when the film is entirely of uncharged atoms (*e.g.*, the platinum films) no such effect occurs and the film has to provide all the photoelectrons, much as thick layers do. It should not be difficult to test out such ideas, *e.g.*, by investigating sodium films on aluminum (the ionization potential of sodium being greater than the work function of aluminum).

5-5. Polarization Selectivity: Alkaline-earth Metals.—Barium, strontium, and calcium have been examined with the result that polarization selectivity and spectral selectivity have been found together for the first two metals, but not for calcium. Pohl's results[3] for a barium mirror are shown in Fig. 5-15. A more elaborate study of the effect with a strontium mirror, formed by evaporation of strontium on to a smooth surface, was made by Dopel.[4] (Although not explicitly stated, the strontium was presumably in the form of a "thick layer" and not a "thin film.") He obtained curves very similar to those given in Fig. 5-15 for angles of incidence ranging from 30 to 75 deg and observed the ratio $I\|/I\perp$ to increase with increasing angle. The maximum for the spectral selectivity occurred at 3400A, while that for barium (Fig. 5-15) occurred at 3600A. The sequence is therefore in the same sense with regard to atomic weights as in the case of the alkali metals. Dopel observed that the $I\|/I\perp$ ratio for strontium at 75 deg dropped from 7.7:1 to 3.7:1 in 20 min, the effect being due to a more rapid decrease in $I\|$ than in $I\perp$.

A peculiar effect was observed in calcium by Pohl and Pringsheim.[5] The spectral distribution curves for the photoelectric current from a calcium mirror with light incident upon it at different angles are given in Fig. 5-16. It will be observed that the slight maximum for 0 deg incidence vanishes completely for higher angles of incidence. On the basis of a subsidiary experiment, which showed that the reflectivity of the calcium mirror diminishes rapidly with decreasing wave-lengths, implying, on optical theory, a deeper penetration of light into the metal, Pohl and Pringsheim offered the following explanation. With perpendicular incidence, the short wave-length light penetrates deeply into the metal and relatively few of the resulting photoelectrons escape; hence the shape

[1] I. Langmuir and K. H. Kingdon, *Proc. Roy. Soc.*, **107**, 61 (1925).
[2] J. A. Becker, *Phys. Rev.*, **28**, 341 (1926); **29**, 364 (1927).
[3] Quoted in Dopel's paper, *Zeits. f. Phys.*, **33**, 237 (1925).
[4] R. Dopel, *Zeits. f. Phys.*, **33**, 237 (1925).
[5] R. Pohl and P. Pringsheim, *Verh. d. Deutsch. Phys. Ges.*, **15**, 111 (1913).

of the curve. With oblique incidence, the absorption takes place in a thinner layer and the electrons have a better chance of escaping.

Studies of the polarization selectivity of the other metals (excepting Hg[1]), belonging to the same column of the periodic table, Mg, Zn, and Cd, do not appear to have been made. As was mentioned in the introduction, Hg shows no polarization selectivity when the amount of light absorbed is taken into account.

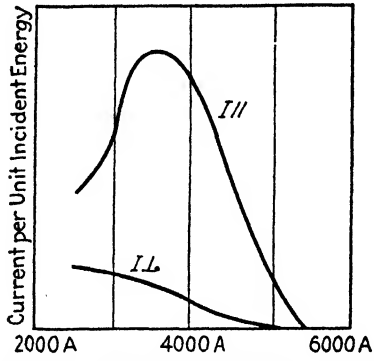

FIG. 5-15.—Selectivity in barium. Angle of incidence = 60 deg.

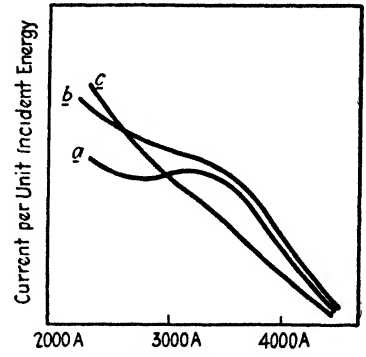

FIG. 5-16.—Calcium. Angle of incidence: (a) 0 deg. (b) 45 deg. (c) 70 deg.

5-6. Polarization Selectivity: Other Metals.—The polarization selectivity of films of Au, Cu, Ag, and Pt, sputtered on to glass, has been investigated by Gross.[2] The photoelectric currents were measured per unit energy of absorbed light and the amount of light absorbed was calculated from the optical constants of the metal. The film thickness was determined by weighing. Curves for gold are shown in Fig. 5-17. It will be seen that there is apparently a marked polarization selectivity, in that $I\|/I\perp$ is not equal to unity for all angles. Similar results were obtained for Cu. The results were ambiguous for Ag and Pt in that both the $I\|$ and $I\perp$ curves increased with the angle, the $I\|$ curve increasing somewhat faster. While a sputtered Cu film shows an increasing $I\|/I\perp$ ratio, as in Fig. 5-17, a film produced by evaporation shows hardly any change. No change in the $I\|/I\perp$ ratio with increasing angle was found for bismuth.

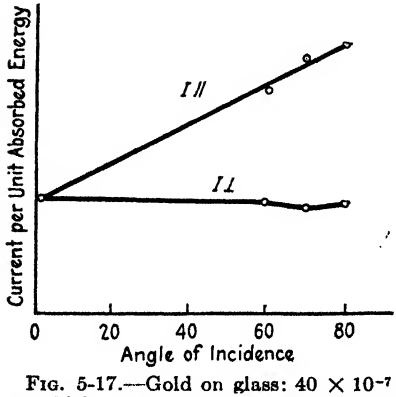

FIG. 5-17.—Gold on glass: 40 × 10^{-7} cm thick. Age, 35 min. Illuminated by 2536A.

[1] R. POHL, *Verh. d. Deutsch. Phys. Ges.*, **10**, 609 (1909).

[2] F. GROSS, *Zeits. f. Phys.*, **6**, 376 (1921); **31**, 637 (1925).

It is certainly questionable whether we can assume that the optical constants obtained experimentally for polished surfaces of metals can be assumed to be characteristic of the same metals produced in other ways, as in these experiments. Before finally accepting these results, it would be very desirable to measure experimentally the amount of light actually absorbed in the metal surfaces actually used in the photoelectric experiments.

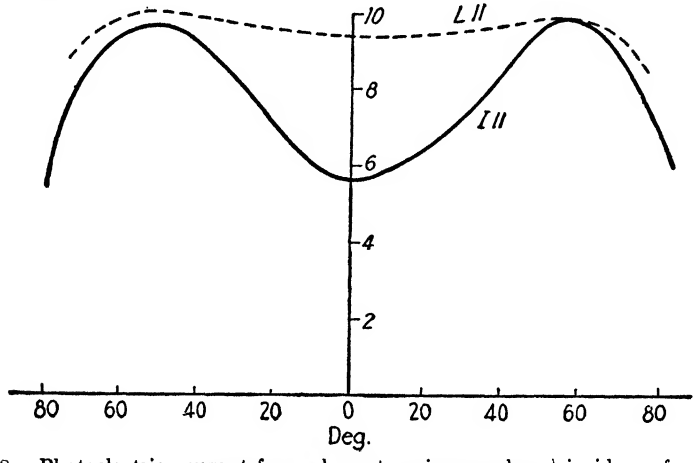

FIG. 5-18.—Photoelectric current from glass at various angles of incidence for $E\|$ light. $L\|$ represents amount of light *absorbed*.

5-7. Polarization Selectivity: Insulators.—Optical theory states that, for $E\|$ light, incident on a glass surface, the amount reflected is

$$J = J_0 \frac{\tan^2(\alpha - \beta)}{\tan^2(\alpha + \beta)},$$

where J_0 is the intensity of the incident light, and α and β are the angles of incidence and refraction. The fraction of the light absorbed is $\left(1 - \frac{J}{J_0}\right)$, which has a maximum at the polarizing angle, *i.e.*, when $\alpha + \beta = 90$ deg. Wehnelt and Schmerwitz[1] investigated the photoelectric currents from a piece of glass, 18 × 18 × 0.13 mm, sooted on the back surface whereby electrical connections could be made to it, as a function of the angle of incidence. Even with the full light from a carbon arc the currents were very feeble, being of the order 10^{-13} amp. The currents obtained are shown in Fig. 5-18. The dotted line, reproduced from a separate curve in the original paper, represents the amount of light absorbed at different angles. It will be noticed that the maximum photoelectric current $I\|$ occurs at the angle (the "polarizing angle") at which the absorption is a maximum. On the other hand, the $I\|$ curve is far from being superposable on the $L\|$ curve, as it should be

[1] A. WEHNELT and G. SCHMERWITZ, *Zeits. f. Phys.*, **57**, 533 (1929).

if the photoelectric current were determined solely by the amount of light absorbed. It may well be, however, that the $L\|$ curve is not correctly computed for the wave-lengths (probably between 2500A and 2000A) actually effective in producing a photoelectric effect in glass, although the coincidence of the $L\|$ and the $I\|$ curves at the polarizing angle suggests that it is not far wrong. Unfortunately, Wehnelt and Schmerwitz do not give any $I\perp$ curves; it would have been very interesting to compare them with the $I\|$ curves.

5-8. Spectral Selectivity with Unpolarized Light.—It is clear from the evidence presented in previous sections that, as a rule, wherever there is an unusual degree of polarization selectivity, there will also be found spectral selectivity. To investigate polarization selectivity the surface must be optically flat; a definite angle of incidence on a granular or matte surface is meaningless for this purpose, because the angle varies at random from one surface element to another. Hence it would be almost futile to investigate polarization selectivity for such surfaces, although we can legitimately examine its spectral selectivity with unpolarized light. When it is possible to make a direct experimental test with polarized light on a specular surface, it is found that a maximum in the spectral distribution curve for unpolarized light is due almost always to the $E\|$ component. If this maximum be pronounced then polarization selectivity is present, *i.e.*, $I\|/I\perp$ is larger than can be accounted for by any possible values of $L\|/L\perp$. On the other hand, slight spectral selectivity, as Ives has shown, need not imply polarization selectivity, *i.e.*, $I\|/I\perp$ may be equal to $L\|/L\perp$. Hence polarization selectivity does not necessarily accompany spectral selectivity, yet when the latter is marked it is possible that polarization selectivity would be present if the surface could be made optically flat. This, then, is the justification for placing a section on Spectral Selectivity with Unpolarized Light in this chapter. In practice, these considerations are limited mainly to the case of the alkali metals.

When the pure alkali metals have been well outgassed and are examined in the usual high-vacuum cell, they all show marked spectral selectivity. (We shall see later that when *extraordinary* care is taken to outgas the metal and the cell, the selectivity disappears, at least in the case of potassium. This, however, calls for a technique which is more elaborate than that ordinarily employed in making "good" vacuum photoelectric cells.) The wave-length at which the spectral maximum is found for such cells changes but little from cell to cell, but the *height* of the maximum varies enormously. Even in the case of a batch of cells prepared under apparently identical conditions, the yield at the maximum may be double as much for one cell as for another.[1] Consequently the spectral selec-

[1] N. R. Campbell and Dorothy Ritchie, "Photoelectric Cells," p. 32 (Sir Isaac Pitman & Sons, 1929).

tivity curves, shown in Fig. 5-19, are arbitrarily adjusted to the same height. Too much reliance must not be put on the shapes of the curves; they are given merely to show the general characteristics.

In Millikan and Souder's experiments,[1] the maximum at 2800A for Li, and that at 3400A for Na, were absent for surfaces newly cut in vacuum; they appeared slowly as the surfaces grew older. Thus the first indication of a maximum appeared after 14 hr; it required 134 days

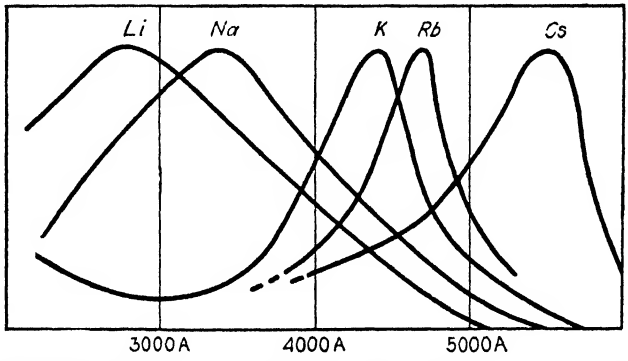

FIG. 5-19.—Spectral selectivity curves for the alkali metals. Li, Na, K, Rb (*Pohl and Pringsheim*). Cs (*Campbell and Ritchie*).

to attain its greatest value. Compton and Richardson[2] also studied cut surfaces of Na, and found, in addition to the known maximum near 3400A, a second one at 2200A. In contrast, however, to the observations of Millikan and Souder, the maxima flattened out in the course of a few hours after a new surface had been exposed by cutting. These results are possibly consistent in the light of our present knowledge that absorption of gas slowly evolved in a cell first brings out a maximum, but eventually suppresses it, if we assume that the vacuum conditions of Compton and Richardson were poorer than those of Millikan and Souder.

Alloying Tl and Hg with K shifts the position of the maximum towards the ultra-violet and reduces its height considerably.[3] Alloys with Bi, Sb, P, and Pb have no maximum.[4]

Pohl and Pringsheim[5] could find no evidence of a spectral selectivity for Tl, Pb, Sn, Cd, and Bi. For Mg, Ca, and Al, however, they[6] found that a newly distilled surface had no spectral selectivity, but after a few hours a marked selectivity appeared, accompanied by a considerable shift of the threshold to the red. The curves for Mg are shown in Fig.

[1] R. A. MILLIKAN and W. H. SOUDER, *Proc. Nat. Acad. Sci.*, **2**, 19 (1916).
[2] K. T. COMPTON and O. W. RICHARDSON, *Phil. Mag.*, **26**, 549 (1913).
[3] R. POHL and P. PRINGSHEIM, *Verh. d. Deutsch. Phys. Ges.*, **12**, 697 (1910).
[4] R. POHL and P. PRINGSHEIM, *Verh. d. Deutsch. Phys. Ges.*, **12**, 1039 (1910).
[5] R. POHL and P. PRINGSHEIM, *Verh. d. Deutsch. Phys. Ges.*, **13**, 474 (1911).
[6] R. POHL and P. PRINGSHEIM, *Verh. d. Deutsch. Phys. Ges.*, **14**, 546 (1912); **15**, 111 (1913).

5-20. (It will be remembered that in another investigation [Sec. 5-5] Pohl and Pringsheim found that the maximum for a Ca mirror with normal incidence was not a spectral selectivity of the same kind as that characteristic of the alkali metals. The nature of the new maxima in Ca, Mg, and Al is therefore somewhat doubtful.) The positions of the maxima of the spectral selectivities are summarized in the Table 5-2.

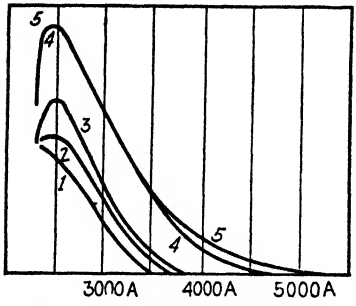

FIG. 5-20.—Spectral selectivity of Mg distilled in vacuum. Age: 1. Few min. 2. 20 min. 3. 1 hr. 4. 5 hr. 5. 24 hr.

It should be stated again that these values are for well-outgassed materials in a good vacuum. But when *extreme* precautions are taken to outgas the material, it has been found recently that the spectral selectivity disappears in potassium. There are no experiments on record in which the same unusual degree

TABLE 5-2.—POSITION OF MAXIMUM SPECTRAL SELECTIVITY

Material	Wave-length at maximum spectral selectivity, A. u.							
	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
Cs					4800	5500	5390	5400
Rb	4700				4600		4730	4810
K	4400				4100		4410	4560
Na	3400		3500, 2250	3400	(see note 9)		4200	4270
Li	2800			2800			4050	
Ba	2800							
Sr		3400						
Mg	2500							
Al			2150					
K-Na alloy	3900				(see note 9)			
Rb-Na alloy					4600			
Rb-K alloy					4600			
Cs-Na alloy					4800			
Cs-K alloy					4900			
Cs-Rb alloy					4800			
K-Hg alloy	3800							
K-Tl alloy	3000							

[1] R. POHL and P. PRINGSHEIM, *Verh. d. Deutsch. Phys. Ges.*, **11**, 1039 (1910); **14**, 546 (1912); **15**, 111 (1913).
[2] R. DOPEL, *Zeits. f. Phys.*, **33**, 237 (1925).
[3] O. W. RICHARDSON and K. T. COMPTON, *Phil. Mag.*, **26**, 549 (1913).
[4] R. A. MILLIKAN and W. H. SOUDER, *Proc. Nat. Acad. Sci.*, **2**, 19 (1916).
[5] H. E. IVES and A. L. JOHNSRUD, *Astrophys. Jour.*, **60**, 231 (1924).
[6] N. R. CAMPBELL, "Photoelectric Cells," p. 32 (Isaac Pitman, 1924).
[7] E. F. SEILER, *Astrophys. Jour.*, **52**, 129 (1920).
[8] *Ibid.*, for surfaces "sensitized" by a glow discharge in H_2.
[9] No maximum was found between 4000A and 6000A.

of outgassing was applied to the other materials, and so we are unable to say whether or not the selectivity would disappear here also.

Ives and Johnsrud[1] give an interesting set of curves (Fig. 5-21) showing how the spectral selectivity for one and the same substance, potassium, differs with the state of the surface. Surface 1 is produced by a glow discharge in hydrogen with the potassium as cathode. The other surfaces are pure, at least in the sense that no gas has been deliberately adsorbed on the surface. Surfaces 3, 4, and 5 were optically reflecting and illuminated by $E\|$ light at 60 deg. The maxima are

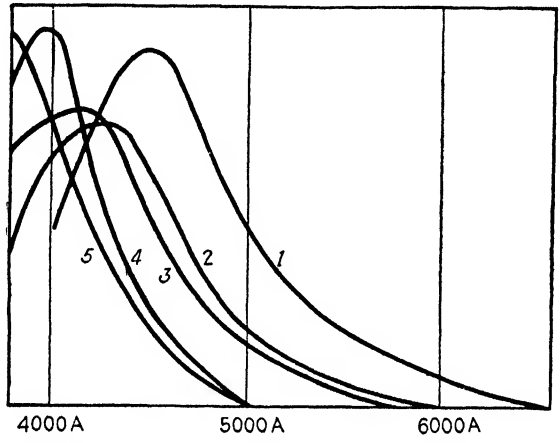

FIG. 5-21.—Spectral selectivity of potassium. 1. Colored colloidal. 2. Matte. 3. Molten. 4. Reflecting layer on glass. 5. "Thin film" on platinum.

evidently in the same sequence as the thresholds, and Richardson's relation, $\nu_{max} = (\frac{8}{5})\nu_0$, holds approximately.

The contact-potential difference between brass and sodium-potassium alloy increases at first rapidly and then more slowly, approaching its final value asymptotically, when observations are made at intervals from the time a fresh surface is exposed.[2] Unfortunately, photoelectric spectral distribution curves were not taken simultaneously; it is not unlikely that a change in the character of the curves would occur along with the shift in the threshold which is known to alter with the contact-potential difference.

5-9. Spectral Selectivity with Polarized Light.—An important contribution to the subject has been made by Fleischer and Dember,[3] who measured experimentally the absorption of the light simultaneously with the measurements of the photoelectric current. The amount of light absorbed was computed from photometric measurements of the light incident on the potassium mirror and the light reflected by it.

[1] H. E. IVES and A. L. JOHNSRUD, *Astrophys. Jour.*, **60**, 231 (1924).

[2] F. WOLF, *Ann. d. Phys.*, **83**, 1000 (1927).

[3] R. FLEISCHER and H. DEMBER, *Zeits. f. Tech. Phys.*, **7**, 133 (1926). Had results with $E\perp$ light also been recorded, allowing a study of the polarization selectivity, Sec. 5-2 would have been the natural place to discuss them.

Solid potassium with a mirror-like surface was illuminated by $E\|$ light incident at 45 deg. The potassium was outgassed with great thoroughness and measurements were taken frequently over a period of 109 days. To avoid confusion only a few curves are reproduced in Fig. 5-22. It is evident that the photoelectric current per unit energy of *incident* light always has a maximum somewhere in the curve, and in the absence of further information as to the amount of light absorbed, one would naturally infer that there was always some degree of spectral selectivity. But in the early stages (the first 35 days), the absorption curves have

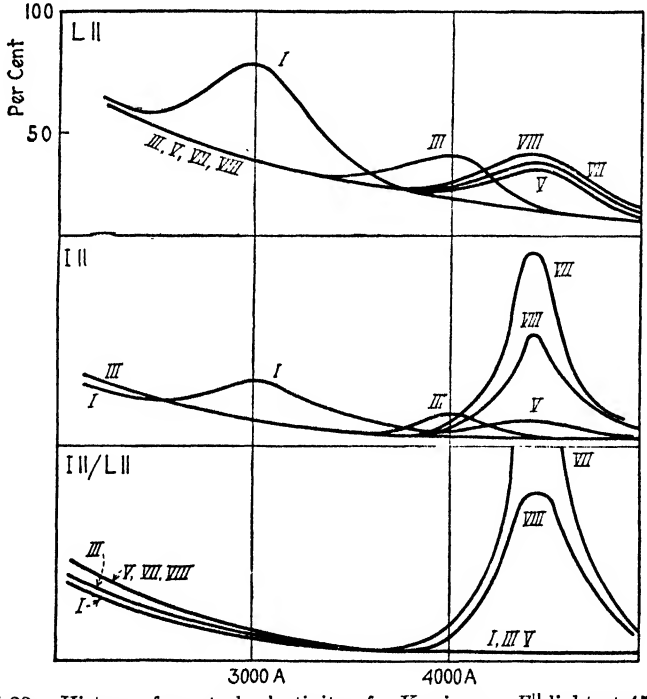

FIG. 5-22.—History of spectral selectivity of a K mirror. $E\|$ light at 45 deg.

	Age, days	
I	1	
III	15	(II, IV, and VI fit in, but omitted for clearness)
V	35	
VII	63	
VIII	109	

maxima at precisely the same places, and, when one curve is divided by the other, so as to obtain the yield in terms of the amount of *absorbed* light, all indications of a maximum vanish. In the later stages we find the appearance of marked spectral selectivity, even when referred to absorbed light, which is most pronounced at 63 days, after which it slowly diminishes. Nothing is said about the yield with $E\perp$ light. It would have been most interesting to see whether the ratios $I\|/L\|$ and $I\perp/L\perp$ were equal in the early stages, or not. Fleischer and Dember attribute the growth of the spectral selectivity, and its subsequent decline, to the

accumulation of gas on the surface of the potassium as it is slowly given off by the walls of the cell. Whether this be the explanation, and it seems to be reasonable, or whether some slow changes in the crystal structure of the surface take place, the results give us, so to speak, a clear-cut moving picture of a phenomenon of which previously we had only occasional snapshots taken at indeterminate stages. The results also show that a selectivity with reference to incident light energy does not always mean a selectivity with respect to the amount of light actually absorbed.

5-10. Spectral Selectivity. Effect of Gases.—The alterations in the spectral selectivity hitherto discussed are very probably associated with the variation in the kind and amount of gas adsorbed on the surface, although it is conceivable that changes in the crystal structure of the surface layers could affect the spectral selectivity. In this section we shall consider experiments in which direct attempts are made to find out the influence of gases. One such successful attempt by Fleischer has already been discussed in Sec. **5-2**, in which it was placed because he used polarized light.

Long-continued outgassing reduces the photoelectric current from potassium enormously (Wiedmann and Hallwachs).[1] As the cell used was of glass, its transparency limit was probably around 3500A, and consequently nothing can be inferred as to the effect in the far ultraviolet. Admission of pure argon or nitrogen has no effect on the sensitivity of the surface.[2] Hydrogen[2] and oxygen[3] both restore the sensitivity. In the latter case, Pohl and Pringsheim found that exposure to too much oxygen diminished the effect, the maximum spectral selectivity being obtained after exposure to oxygen at 0.85 mm. More recent work (Fleischer) on the effect of hydrogen and oxygen on the selectivities has been discussed in Sec. **5-2**. Pohl and Pringsheim found the maximum in the spectral selectivity of potassium exposed to oxygen to be at 4050A, but the more recent researches of Wiedmann and of Fleischer agree in placing it at 3130A.

Fleischer and Teichmann[4] found that exposing a K surface, having a strong characteristic maximum at 4400A, to various gases, in general,

[1] G. Wiedmann and W. Hallwachs, *Verh. d. Deutsch. Phys Ges.*, **16**, 107 (1914); G. Wiedmann, *Verh. d. Deutsch. Phys. Ges.*, **17**, 343 (1915). It should be stated that Pohl and Pringsheim, and Ives, Dushman, and Karrer were unable to confirm this conclusion. The recent work of Fleischer (Sec. **5-2**), Fleischer and Dember (Sec. **5-9**), and Fleischer and Teichmann (Sec. **5-10**) shows definitely that a thoroughly outgassed K surface has a considerably smaller photoelectric effect than one which has not been so well outgassed. The maximum effect is obtained after exposure to a minute trace of gas; more than this often brings about a great reduction.

[2] G. Wiedmann, *Verh. d. Deutsch. Phys. Ges.*, **18**, 337 (1916).

[3] R. Pohl and P. Pringsheim, *Verh. d. Deutsch. Phys. Ges.*, **15**, 625 (1913); L. R. Koller, *Phys. Rev.*, **29**, 902 (1927).

[4] R. Fleischer and H. Teichmann, *Zeits. f. Phys.*, **60**, 317 (1930); **67**, 184 (1931).

reduced the photoelectric effect and shifted the position of maximum sensitivity to another wave-length. This wave-length was found to be at 3130A, 3340A, 3650A, and 3650A, after the K had been exposed to O_2, NO, NO_2, and N_2, respectively.

A short statement of this kind, however, fails to indicate the complexity of the situation and the necessity for describing precisely the conditions under which these values were obtained. For example, we stated earlier in this section that, according to one research, N_2 had no effect on the photoelectric sensitivity of K, whereas according to the research now under consideration, it has an effect. As a second example, also from this research, exposure of a well-outgassed K surface to NO at 0.1 mm for a few minutes reduces the sensitivity about fifteen times, but after standing in a high vacuum for several hours the sensitivity increases until it is about three times as high as it was originally.

The recovery of the large photoelectric emission of potassium, which had been made relatively insensitive by thorough outgassing,

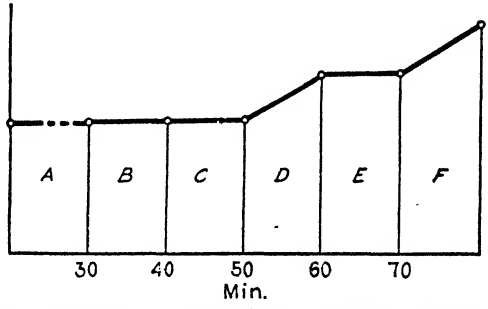

FIG. 5-23.—Effect of hydrogen on photoelectric emission from potassium. *A*. Exposure to H_2; no discharge. *B*. H_2 bombarded by 6 volt electrons; K at ground. *C*. H_2 bombarded by 10 volt electrons; K at ground. *D* and *F*. H_2 bombarded by 30 volt electrons; K at -130 volts. *E*. H_2 bombarded by 30 volt electrons; K at ground. (Positive ions reach the K only in cases *D* and *F*.)

on exposure to hydrogen is due to hydrogen ions striking the potassium according to Suhrmann.[1] A thick layer of well-outgassed potassium was distilled on to a platinum strip. Admission of molecular hydrogen produces no change. A discharge through the hydrogen between near-by electrodes has no effect, unless the polarity of the potassium is such as to allow hydrogen ions to strike it. The sequence of experiments supporting this view is shown in Fig. 5-23.

As an alternative to the mechanism suggested by Suhrmann, Fleischer[2] and Campbell[3] believe that interaction between potassium *vapor* and the hydrogen is necessary to bring about the strong spectral selectivity. A very instructive investigation in support of this view has been carried out

[1] R. SUHRMANN, *Phys. Zeits.*, **29**, 811 (1928); R. SUHRMANN and H. THEISSING., *Zeits. f. Phys.*, **52**, 453 (1928); see also O. W. RICHARDSON and A. F. A. YOUNG, *Proc. Roy. Soc.*, **107**, 377 (1925).

[2] R. FLEISCHER, *Phys. Zeits.*, **30**, 320 (1929).

[3] N. R. CAMPBELL, *Phys. Zeits.*, **30**, 357 (1929).

recently by Fleischer and Teichmann.[1] They studied the spectral selectivity for (1) a thoroughly outgassed layer of potassium before and after exposure to hydrogen, (2) a layer of potassium saturated with hydrogen

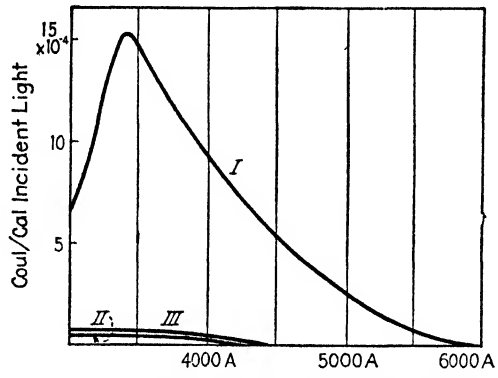

FIG. 5-24.—I. Spectral selectivity of thoroughly outgassed K. II. Spectral selectivity after exposure to 15 mm H_2 for 15 min. III. Spectral selectivity after exposure to 15 mm H_2 for 24 hr.

on top of which was distilled some thoroughly outgassed potassium, and (3) a layer of potassium evaporated, in the presence of hydrogen, from an outgassed source. The spectral selectivity curve for thoroughly outgassed potassium is I in Fig. 5-24. (Note: the maximum at 3340A

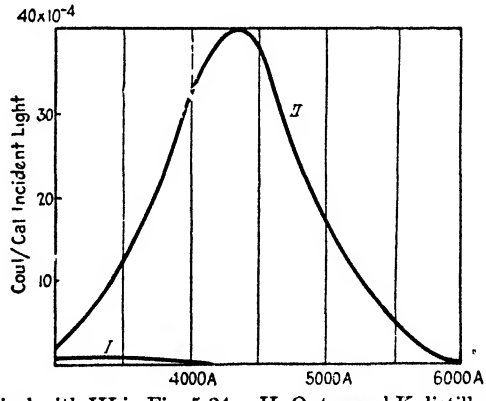

FIG. 5-25.—I. Identical with III in Fig. 5-24. II. Outgassed K distilled on to K saturated with H_2.

is consistent with previous results when we remember that the ordinates are coulombs per calorie of *incident* light. This maximum according to Fleischer's earlier work, already discussed in Sec. **5-2**, disappears when the amount of *absorbed* light is taken into account.)

[1] R. FLEISCHER and H. TEICHMANN, *Zeits. f. Phys.*, **61**, 227 (1930).

1. The effect of admitting a considerable amount of hydrogen is to diminish the current greatly (curves II and III). (It is probably needless to say that the photoelectric currents were always measured after removing the hydrogen.)

2. The next experiment was to begin with the potassium which had been saturated with hydrogen by exposure to it for 24 hr and to distill on to it, in a good vacuum, some thoroughly outgassed potassium. We now find the familiar 4400A maximum (Fig. 5-25).

3. The same maximum was again obtained when thoroughly outgassed K was distilled on to the cathode in the presence of hydrogen at 10^{-2} mm.

In experiments 2 and 3, leading to the 4400A maximum, potassium vapor interacted either with gaseous hydrogen or with hydrogen already adsorbed in the first layer. Experiment 1 implies that, in the absence of potassium vapor interacting with hydrogen, no 4400A maximum appears. This conclusion would have carried more conviction had the authors repeated the experiment with considerably less hydrogen, for there is indirect evidence that but a very small amount is necessary to bring out the 4400A maximum and that more tends to diminish it. Fleischer and Teichmann were unable to verify Suhrmann's experiment with hydrogen ions.

By examining the reflection of electrons at surfaces of potassium treated in various ways, Kluge and Rupp[1] have found some interesting correlations between the magnitude of the selective effect and the nature of the surface. Bragg's formula for the reflection of X-rays by crystals applies equally well to the reflection of a beam of electrons at crystal surfaces, when the wave-length λ of the X-rays and the velocity v of the electrons are related by the formula $\lambda = h/mv$, where h is Planck's constant and m the mass of the electron. Since the electron reflection occurs within an exceedingly thin surface layer, it is obvious why we may expect electron reflection experiments to give more useful information than X-ray-reflection experiments as to the state of that part of the surface which is of photoelectric significance. The investigation was carried out in the following way: Gas-free potassium was distilled on to a flat surface until the layer was just thick enough to be opaque (state *a*). It was then exposed to hydrogen at a low pressure for a few minutes (*b*), then exposed to a glow discharge through hydrogen (*c*), and finally exposed to a stronger glow discharge (*d*). For each state of the surface, a photoelectric spectral distribution curve and an electron reflection curve were obtained. In the electron reflection experiments a beam of electrons of known velocity was directed at the surface, the angle of incidence being 60 deg. A collector was so placed as to receive only those electrons which were reflected at 60 deg. The number of electrons entering the collector was measured as the velocity of the primary beam

[1] W. Kluge and E. Rupp, *Phys. Zeits.*, **32**, 163 (1931).

was increased by small steps. In general, curves with a number of distinct peaks were obtained. The surface may be regarded as being made of many tiny crystals orientated at random, just as in a "powdered crystal" in X-ray investigations. It should, therefore, be possible to get reflections from all planes provided the equivalent wave-length of the electron beam satisfies the Bragg formula. The peaks in the curves then correspond to various reflecting planes and various orders of reflection. From X-ray data it is known that potassium is built on a cubic lattice with a (100) spacing of 5.20A. It is therefore possible to predict the equivalent wave-length, or the velocity, of the electron beam reflected by the (100), the (110), and the (111) planes for various orders of reflection. In

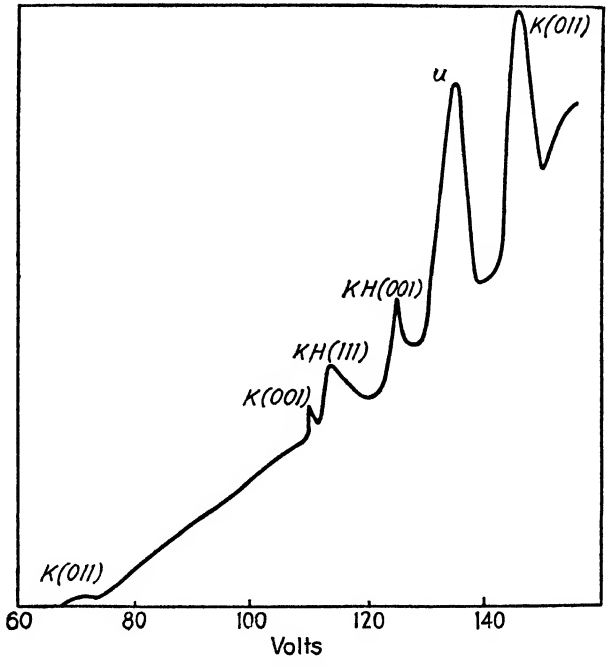

FIG. 5-26.—Electron reflection at a K surface

this way, certain peaks (12 in all) could be attributed to K, provided that we assign to the K crystal a "surface potential jump" (Sommerfeld's W_a, Sec. **6-21**), amounting to 7.3 volts. Other peaks (8 in all) were assigned to a cubic crystal whose spacing was 5.40A, presumably the KH crystal. Four other peaks were attributed to a set of planes only 2.9A apart; it was not possible to identify the substance responsible for these peaks. A typical electron reflection curve is shown in Fig. 5-26. The results for the K surface in the various states are summarized in Table 5-3. The third column contains the inferences from the electron reflection experiments.

TABLE 5-3.—ELECTRON REFLECTION BY POTASSIUM SURFACES

Surface	Color	Crystals in surface	Selective effect	Inferred size of K particles
(*a*) Pure K	Metallic	K	Weak	
(*b*) Exposed to H_2	Metallic	KH alone	Somewhat stronger	Very small (atomic)
(*c*) Glow discharge in H_2	Reddish-violet	KH; K (small)	Strong	Small (molecular)
(*d*) Stronger glow discharge in H_2	Green	K and KH	Weaker	Larger

It is obvious that the effect of mere contact with H_2 is to change the surface layer to KH. It is assumed that free, isolated K atoms must be embedded in or on the layer to account for the photoelectric effect, since pure KH is inactive photoelectrically (Elster and Geitel) and since particles of K would give a set of peaks characteristic of its lattice. A glow discharge causes small aggregations of K to form and it is evident that the maximum photoelectric sensitivity is attained when these are not too large.

Suhrmann[1] observed that exposing a K surface, showing a selective effect, to a vapor (naphthalene) which reacted feebly with it and to a vapor (paraffin) which did not react with it, gave different results. In the first case, the first trace of vapor suppressed the selective maximum, leaving only the normal curve; more vapor caused the effect to disappear altogether. Admission of a little K vapor brought back a strong selective effect. In the second case, the curve was merely reduced by the same proportional amount throughout the spectrum, leaving the selective characteristics unaffected. Admission of a little K vapor did not bring back the strong selective effect. Suhrmann interpreted this result to indicate that a strong selective effect was conditioned by a chemical reactivity between the K and the layer on which it was deposited.

Kluge[2] found that spectral selectivity could be produced by exposing K to the O_2-like elements S, Se, and Te. The maxima came at 3130A for O_2, 4120A for S, 4125A for Se, and 4300A for Te. Kluge suggests that the spectral selectivity is to be associated with the presence of colloidal particles of K embedded in or on the compound (*e.g.*, K_2S) but that the compound has some effect on the position of the maximum.

It is of interest to record the highest yields which have been obtained with various surfaces at the peaks of their respective spectral distribution curves. Pohl and Pringsheim obtained 3×10^{-2} coul/cal, Suhrmann and Theissing obtained 5.6×10^{-2} coul/cal, and Campbell records several yields around 3×10^{-2} coul/cal. These are all for potassium surfaces and they are calculated in terms of the energy of the incident light. Taking the wave-length of the selective maximum to be at 4400A, the

[1] R. SUHRMANN, *Phys. Zeits.*, **32**, 216 (1931).
[2] W. KLUGE, *Zeits. f. Phys.*, **67**, 497 (1931).

5.6×10^{-2} coul/cal means that one electron is emitted from the surface for every 14 quanta incident upon it! Lazlo[1] mentions a yield of 5.2×10^{-2} coul/cal for magnesium at its maximum at 2536A. He does not state whether any special steps were taken to obtain this remarkably high yield, a yield hitherto obtained only with alkali metals under special conditions. Richardson and Rogers[2] record maximum yields for platinum and aluminum as 3×10^{-5} and 10×10^{-5} coul/cal, respectively. They also state that the yield of sodium at its maximum is 47×10^{-4} coul/cal.

An interesting attempt to measure the yield in terms of *absorbed* light, instead of *incident* light has been made by Fleischer.[3] He used a semitransparent gold leaf mounted on a tube so that the quantity of light transmitted by it could be measured. Potassium was vaporized in a side tube and allowed to condense on the gold leaf until the maximum photoelectric emission was obtained. The potassium film was found to absorb about 4 per cent of the active light over and above the amount absorbed by the gold leaf. The photoelectric yield amounted to 38×10^{-2} coul/cal of light absorbed by the potassium, which corresponds to the emission of one electron for every four quanta absorbed! (This mode of presenting the results tacitly assumes, of course, that all the photoelectrons are due to the additional absorption by the potassium film, and originate in the film. If, however, one regards the principal function of the film as the lowering of the work function of the surface as a whole, so that the photoelectrons come from the gold leaf as well as from the potassium film, then the total amount of light absorbed would have to be taken into consideration.)

5-11. Spectral Selectivity: Sensitized Surfaces and Composite Films. The photoelectric yield can be considerably increased by the process known as *sensitization*, discovered by Elster and Geitel.[4] At first they converted the alkali metal, by heating it in hydrogen at 350°C, into a colorless crystalline hydride which was quite insensitive photoelectrically to visible light. On bombarding it with cathode rays the surface became brightly colored and acquired a photoelectric sensitivity much exceeding that of the pure metal. Later they found this procedure to be unnecessary; the same increase in sensitivity could be attained by passing a glow discharge through hydrogen in contact with the alkali metal. The sensitized surfaces have characteristic colors quite different from the

[1] H. DE LAZLO, mentioned in "Photoelectric Cells and Their Applications," p. 222 (The Physical and Optical Societies of London, 1930).

[2] O. W. RICHARDSON and F. J. ROGERS, *Phil. Mag.*, 29, 618 (1915).

[3] R. FLEISCHER, *Phys. Zeits.*, **32**, 217 (1931).

[4] J. ELSTER and H. GEITEL, *Phys. Zeits.*, **11**, 257, 1082 (1910); **12**, 609 (1911); R. POHL and P. PRINGSHEIM, *Verh. d. Deutsch. Phys. Ges.*, **13**, 211 (1911); **15**, 179 (1913); W. B. NOTTINGHAM, *Jour. Franklin Inst.*, **206**, 637 (1928); N. R. CAMPBELL, *Phys. Zeits.*, **30**, 537 (1929).

silvery appearance of the pure metals: blue-violet for K, pale blue-violet for Rb, green for Cs, and brown for Na. The appearance of the metal surfaces so sensitized suggested to Elster and Geitel the idea that they were composed of colloidal particles of alkali metal dissolved in the hydride. Hence, cells of this kind are frequently referred to as "hydride" cells or as "colloidal metal" cells. It is perhaps better to regard these names as identification labels rather than as implying an ascertained process. In fact, there is considerable uncertainty as to the best way of preparing highly sensitive surfaces; thus Nottingham[1] makes cells with characteristics which are permanent by passing the glow discharge for a second or two, while Campbell and Ritchie[2] imply that it is better to pass the discharge for an hour or more. Whether or not to take great precautions in purifying the metal initially and whether or not to make the alkali metal the cathode or anode in the glow discharge seem to be matters of personal taste. A typical improvement in the photoelectric yield due to sensitization is shown in Fig. 5-27 (Campbell and Ritchie[2]). Sensitization by a H_2 discharge does not alter greatly the position of the maximum (see Columns 7 and 8 in Table 5-2). Elster and Geitel, and Pohl and Pringsheim have obtained extremely high yields with sensitized alkali metals of the order of 3×10^{-2} coul/cal. The work of Fleischer and others, already discussed, shows that, in the case of potassium, contact between hydrogen and potassium (or potassium vapor) under certain conditions leads to a comparable increase in sensitivity with a maximum at about the same wave-length—4400A. We are therefore inclined to think that the glow discharge in hydrogen is merely a convenient practical way of producing the same surface change—whatever that may be—as results from mere contact with hydrogen in the researches referred to.

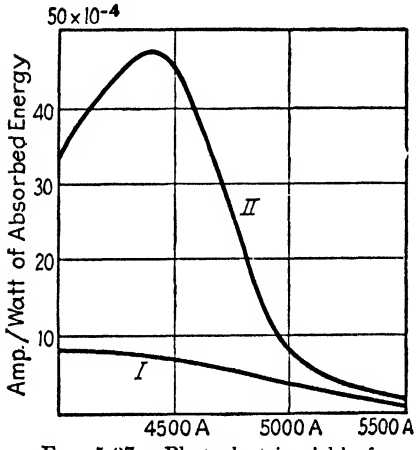

FIG. 5-27.—Photoelectric yield of potassium. I. Before sensitization. II. After sensitization.

The results as to the effect of an electric discharge on the photoelectric yield of metals outside the alkali metals are conflicting.[3] Considerable changes occur, but according to the older results, here cited, the direction

[1] W. B. NOTTINGHAM, *Jour. Franklin Inst.*, **206**, 637 (1928).

[2] N. R. CAMPBELL and DOROTHY RITCHIE, "Photoelectric Cells," p. 32 (Sir Isaac Pitman & Sons, 1929).

[3] W. F. HOLMAN, *Phys. Rev.*, **25**, 81 (1907); V. L. CHRISLER, *Phys. Rev.*, **27**, 267 (1908).

of the discharge is important, the authors referred to, however, disagreeing as to which direction increases or decreases the yield. In a recent investigation, in which a sensitive photoelectric cell was needed for measuring feeble monochromatic light (2536A) in the ultra-violet, Thomas[1] improved the sensitivity of the aluminum plate in his cell seventy-five times by making it a cathode in a hydrogen discharge. There was no noticeable shift of the threshold into the visible.

Since 1928 a number of remarkably interesting discoveries have been made in which suitable modifications of the "thin films" studied by Ives displace the thresholds towards the infra-red, and increase the yield, especially in the new long wave-length region. Campbell[2] found that sensitizing the invisible thin film of alkali metal, which was left when the rest of the "thick layer" had been distilled away by moderate heating, with a glow discharge in hydrogen, resulted in a surface possessing a remarkable sensitivity in the red. Table 5-4 shows first the effect of sensitizing a thick layer by a glow discharge (the effect already discussed earlier in this section), and secondly the effect of sensitizing the invisible thin film. The nature of the supporting metal (or perhaps its oxide film) is important, for the photoelectric current from a thin film of K on Cu was eight times that from a thin film of K on Ag.

TABLE 5-4.—EFFECT OF SENSITIZATION ON POTASSIUM SURFACES

State	Photoelectric current	
	Blue light	Red light
(*A*) Thick layer on Ag	70	1
(*A'*) Thick layer on Ag, sensitized	480	3
(*B*) Thin film on Ag	400	23
(*B'*) Thin film on Ag, sensitized	450	600

Surfaces with a remarkably high yield and a hitherto unattained sensitivity in the red and infra-red have been produced by supporting a thin film of Cs on a specially treated base. Cells containing such surfaces are of great value in many technical fields. The yield and spectral distribution depend vitally on the way in which the surface is made. One form of surface is made in the following way.[3] A cell, containing a silver deposit on its inside walls, or containing a silver-plated cathode not in contact with the walls, is heated in the presence of O_2 and then cooled, after which the surplus gas is pumped out. Cs vapor is now admitted and the cell is heated to 300°C. The photoelectric

[1] A. R. THOMAS, *Phys. Rev.*, **35**, 1253 (1930).

[2] N. R. CAMPBELL, *Phil. Mag.*, **6**, 633 (1928).

[3] L. R. KOLLER, *Phys. Rev.*, **36**, 1639 (1930); see also *Jour. Opt. Soc. Amer.*, **19**, 135 (1929) and *Gen. Elec. Rev.*, **31**, 476 (1928).

sensitivity increases towards a flat maximum; the heating is stopped when the sensitivity is about to decrease. The spectral distribution curve is shown in Fig. 5-28 (curve II). (Other surfaces involving Cs are put in for comparison.) This type of cell is called by Koller a Cs-O-Ag cell; we shall refer to it as a type 1 cell. The high temperature drives off all the Cs except for the last atomic layer or two, which are very adherent (Sec. **5-4**). A second type of surface, $Cs\text{-}Cs_2O\text{-}Ag$, is made by actually oxidizing the Ag surface before admitting the Cs.[1] According to Campbell,[2] this is effected by passing a discharge through oxygen

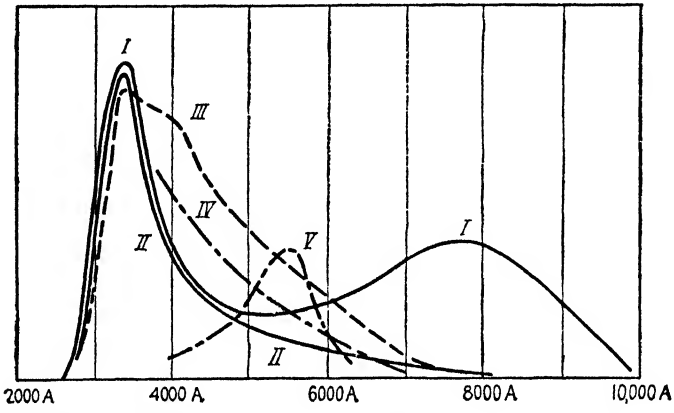

FIG. 5-28.—Spectral distribution curves of caesium. I. Cs on Cs oxide on Ag (*Koller*) (type 2). II. Cs on O_2 on Ag (*Koller*) (type 1). III. Cs on Mg (*Zworykin*). IV. Cs ("thin film") on Pt (*Ives*). V. Cs (pure, thick layer) (*Seiler*). (All per unit energy incident light.)

at a few millimeters pressure in contact with the Ag surface. The process is discontinued when a certain blue color is obtained corresponding to an oxidized layer over 10 molecules thick.[3] Cs vapor is now admitted to the cell, which is kept at 200 to 250°C, and a reaction takes place in which Ag_2O is reduced and Cs_2O is formed. If the photoelectric effect (or the thermionic emission) be watched during this process it will be found that, at a certain stage, it will rise rapidly to a maximum. This is believed to be concurrent with the replacement of the Ag_2O by Cs_2O and the appearance of a monatomic film of Cs on the outside. To insure

[1] The difference between the base in type 1 cells and that in type 2 cells is that in the former case oxygen is merely adsorbed on the surface, while in the latter case actual oxidation of the silver is effected.

[2] We wish to thank Dr. N. R. Campbell for sending us information which has not yet been published. See also N. R. Campbell and Dorothy Ritchie, "Photoelectric Cells," p. 34 (Sir Isaac Pitman & Sons, 1929), and the article by N. R. Campbell in "Photoelectric Cells and Their Applications," p. 14 (The Physical and Optical Societies of London, 1930).

[3] Koller uses a layer of oxide which he estimates to be several hundred molecules thick.

a high photoelectric sensitivity the amount of Cs admitted has to be carefully controlled. Too much of it builds up a thick outer layer of Cs, which gives merely the sensitivity characteristic of Cs in bulk. A quantitative study of the amounts of Cs and O_2 used in making a type 2 cell led Campbell to the definite conclusion that the oxide involved is Cs_2O. De Boer and Teves[1] state that the oxide is probably Cs_2O, on the ground that this is stable in the presence of free Cs. On the other hand, Koller's experiments lead him to conclude that the oxide is a suboxide in which there is perhaps from four to six times as much Cs as there is in Cs_2O. The yield of surfaces prepared in this way (type 2) is about 20×10^{-6} amp/lumen, with a source at 2400°K (Koller). Both Koller and Campbell believe that one characteristic of a type 2 surface is the presence of a monatomic layer of Cs on top of an oxide of Cs. (It is supposed that, in a type 1 cell, on the other hand, the O_2 adsorbed on the Ag surface remains uncombined when a Cs film is formed on top of it.) The spectral distribution curves of the two types of surface as determined by Koller[2] are given in Fig. 5-28. Ballard[3] states that the threshold of a type 2 surface is near 12,000A.

It is significant that both Koller and Campbell find that a Cs_2O layer prepared by direct oxidation of Cs will *not* give a type 2 surface with its characteristic high sensitivity. To secure such a surface it is necessary for the Cs_2O to be formed by reduction of Ag_2O by Cs. Campbell believes that this indicates that the latter process insures the proper kind of continuity with the Ag base which is not obtained by the first process. Campbell suggests that the type 2 surface should be represented by the symbol Cs-Cs_2O-Cs-Ag rather than by Cs-Cs_2O-Ag. Koller states that the base does not have to be Ag; any other metal will do, provided that it is properly oxidized. No information is given as to how this oxidation should be effected.

De Boer and Teves[4] deposited a layer of Cs on a Ag base, then oxidized it by exposure to dry O_2, after which enough Cs was admitted to reduce all the higher oxides to Cs_2O and presumably to leave a monatomic layer of Cs on the outer surface. With such a surface a yield of 12×10^{-6} amp/lumen was obtained, a value which is comparable with Koller's and Campbell's most sensitive type 2 surface. This is a puzzling result, for de Boer and Teves produced their Cs_2O by direct oxidation of Cs, a procedure which according to Koller and Campbell does not give the characteristic high yield of Cs-Cs_2O-Ag cells. De Boer and Teves found that a surface with a monomolecular layer of Cs_2O gave the same spectral distribution—that of a type 2 cell—as a surface with a thicker layer of Cs_2O.

Because of the effect of oxygen and hydrogen in modifying so profoundly the photoelectric yield of thin films of alkali metals, Olpin[5]

[1] J. H. de Boer and M. C. Teves, *Zeits. f. Phys.*, **65**, 489 (1930).
[2] L. R. Koller, *Jour. Opt. Soc. Amer.*, **19**, 135 (1929).
[3] J. Ballard, *Jour. Opt. Soc. Amer.*, **20**, 618 (1930).
[4] J. H. de Boer and M. C. Teves, *Zeits. f. Phys.*, **65**, 489 (1930).
[5] A. R. Olpin, *Phys. Rev.*, **36**, 251 (1930).

investigated the effect of substituting other substances for these two gases. He tried a wide variety of substances: oxygen, water vapor, sulphur vapor, sulphur dioxide, hydrogen sulphide, air, sodium bisulphite, carbon bisulphide representing inorganic substances; methyl alcohol, acetic acid, benzene, nitrobenzene, acetone, among organic substances; rosaniline base, eosine, cyanine, kryptocyanine, dicyanine, among organic dyes. Strange to say, almost every substance produced an increase in the sensitivity of the alkali metal to red light. It did not seem to matter whether the substance was inert to the alkali metal, such as benzene, or strongly reactant towards it, such as water vapor. This led Olpin to question whether the increase in the activity was not really due to some material, minute in amount, common to all the substances used. In view of the difficulty of removing the last traces of water from chemicals—heating the chemical was impracticable in many cases—it is conceivable that water vapor was present in all cases, though Olpin believes that the observed effects cannot all be attributed to it.

Beginning with a thick layer of potassium in each case, Olpin (1) sensitized a K surface by the usual glow discharge in hydrogen, (2) exposed another clean K surface to a trace of S vapor, and (3) exposed the last mentioned KS surface to a glow discharge in hydrogen. The results are given in Table 5-5.

TABLE 5-5.—EFFECT OF SULPHUR ON PHOTOELECTRIC SENSITIVITY

Color of light	(1) KH	(2) KS	(3) KSH
White	374	374	374
Violet	20	11	11
Blue	132	101	93
Green	44	85	59
Yellow	9	72	120
Red	1	11	58

The currents were adjusted to equality for white light.

It is evident that surface 3 (KSH) is relatively more sensitive to the red end of the spectrum. Olpin found that proper exposure to sulphur vapor increases the sensitivity of K, Rb, and Cs. Certain Cs surfaces so treated develop a remarkable spectral selectivity in the red and infrared with a maximum near 7500A. As conditions were more easily controlled with sodium, the majority of experiments were carried out with sodium surfaces. The spectral selectivity of a sodium surface was, perhaps strange to say, shifted farther to the red than that of a potassium surface. By depositing a thin film of Na on top of a surface of sodium already exposed to sulphur, a remarkable increase in sensitivity was observed (Fig. 5-29). A still more remarkable effect was obtained by admitting air to the cell (after which it is totally insensitive) and then

distilling a thin film of Na on top of the last surface. The sensitivity now extends to 10,000A. (The curve is shown in Fig. 5-29 as a dotted line, because, in the original paper, this curve is shown in a separate diagram and the relation of the scales is not stated.) The exposure of a potassium surface to H_2, S, SO_2, H_2S, H_2O, S + O, Te, P, and I resulted in substantially the same spectral distribution curves with maxima close to 4400A. Such was not the case with a sodium surface. Here NaS-air, NaSe-air, NaO + S, and NaO surfaces showed a very great relative increase in sensitivity in the region 4500 to 7500A over the sensitivity for NaH, $NaSO_2$, and NaS surfaces.[1] (The symbols merely indicate the sub-

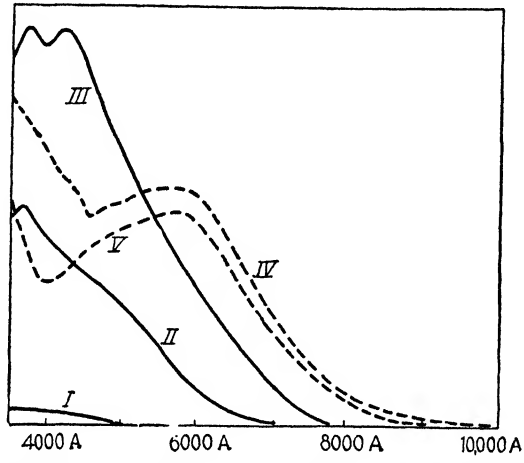

FIG. 5-29.—Spectral selectivity. I. Na surface. II. NaS surface. III. NaSNa surface. IV. NaS-air-Na surface. V. Na-kryptocyanine surface. The units of IV and V are not the same as those of I, II, and III.

stances to which the sodium surfaces were exposed.) Whenever small quantities of dyes were allowed to condense on a potassium or sodium surface, an increase in the sensitivity, especially in the long wave-length region resulted, and this increase was enhanced by condensing a thin film of the metal on top of the modified surface. The most considerable modification was produced by kryptocyanine (Fig. 5-29). Finally the yield is stated to be "as high as 7 microamp per lumen of white light of color temperature 2848°K for sodium cells and to be far higher for caesium cells." It would have been interesting to have the results expressed in coulombs per calorie at each wave-length.

Thus we have a large mass of empirical data, all accumulated since 1928, as to the production of surfaces of high sensitivity, especially in the long wave-length region, by manipulating thin films of alkali

[1] Similar results have been obtained by Selényi for Na treated with O_2, although the gain in sensitivity is apparently considerably less than in Olpin's work. (Selényi, "Photoelectric Cells and Their Applications," p. 25; *cf.* footnote 1, p. 171.)

metals in combination with thin films of an amazing variety of apparently unrelated substances. As Olpin suggests, it is conceivable that these substances act as the vehicle for some unidentified substance which is the active agent, but the evidence for and against this is inconclusive. The excessively small amounts of material involved make it almost impossible to identify them. It is probable that the field will develop rapidly from the point of view of producing dependable cells of high sensitivity, but no convincing theory as to why these effects happen is in sight.[1]

5-12. Thresholds.—Conditions which bring about an accentuation of the spectral selectivity, as a general rule, also produce a shift in the threshold towards the red. We shall consider "thick layers" first.

Millikan and Souder[2] found that a shift in the threshold from 4500A to 5000A accompanied the slow development (134 days) of the spectral selectivity in lithium. Similar results were obtained by Pohl and Pringsheim[3] with magnesium, except that here the changes took place within 24 hr (Fig. 5-20). The displacement of the threshold of potassium to the red as suitable exposure to hydrogen brings out a spectral selectivity, and its return as further exposure to hydrogen suppresses the maximum, is well shown in the work of Fleischer and Teichmann[4] (Figs. 5-24 and 5-25). We also find a rough correspondence between the threshold wave-length and that of the selective maximum, in that they shift together for potassium surfaces prepared in different ways (Ives and Johnsrud,[5] Fig. 5-21).

A careful examination of the shifts in the thresholds of "thin films" of alkali metals as a function of the amount of metal present has been carried out by Ives and Olpin.[6] The thickness of the film was controlled by suitably heating the supporting metal, the rest of the cell being cooled by liquid air, and also by allowing the alkali metal to deposit slowly, at room temperature (or below it) on the supporting metal, from which the deposit had previously been driven off by heating. In every case, no matter whether the film was building up or disappearing, the maximum excursion of the threshold to the red was perfectly definite and character-

[1] Since this section was written, the following papers on related topics have appeared. "The Applicability of Photoelectric Cells to Colorimetry" by H. E. Ives and E. F. Kingsbury (*Jour. Opt. Soc. Amer.*, **21**, 541 [1931]); "The Wave-length Sensitivity of CsO Cells; a New Instrument for the Ultra-violet" by T. F. Young and W. C. Pierce (*Jour. Opt. Soc. Amer.*, **21**, 497 [1931]); "Photocell Theory and Practice" by V. K. Zworykin (*Jour. Franklin Inst.*, **212**, 1 [1931]); "The Effect of Adsorbed K^+ Ions on the Photoelectric Threshold of Fe" by A. K. Brewer (*Phys. Rev.*, **38**, 401 [1931]).

[2] R. A. Millikan and W. H. Souder, *Proc. Nat. Acad. Sci.*, **2**, 19 (1916).

[3] R. Pohl and P. Pringsheim, *Verh. d. Deutsch. Phys. Ges.*, **14**, 546 (1912); **15**, 111 (1913).

[4] R. Fleischer and H. Teichmann, *Zeits. f. Phys.*, **61**, 227 (1930).

[5] H. E. Ives and A. L. Johnsrud, *Astrophys. Jour.*, **60**, 231 (1924).

[6] H. E. Ives and A. R. Olpin, *Phys. Rev.*, **34**, 117 (1929).

istic of the metal. The wave-lengths were as follows: 5900A for Na, 7700A for K, 7950A for Rb, and 8900A for Cs. These values are remarkably close to the wave-lengths of the first lines of the principal series for these elements. To test whether or not this was more than a mere coincidence, Ives and Olpin developed a technique for handling lithium and examined the threshold shift in this case. Lithium, while considerably less electropositive than Na and the rest of the alkali metals, happens to have the first line of its principal series between those of Na and K. Consequently, an identification of the maximum threshold shift for Li with its first principal series line was to be regarded as strong evidence against a mere coincidence. Experiment showed that the maximum excursion was to 6700A, which is practically identical with 6708A, the wave-length of the first line of the principal series of lithium. These are undoubtedly striking results. It is difficult, however, to see why a relationship should exist between the amount of energy necessary to *excite* a free atom and the amount necessary to allow an electron to *escape* from a surface incompletely covered by the same atoms. Campbell[1] maintains that the results just discussed do not hold when the supporting surface is not "clean." Thus a Cs-CsO-Ag surface has a threshold which is around 10,000A. Olpin's work[2] on composite films of alkali metals and such substances as S, Se, H, etc., shows that thresholds far beyond the wave-lengths of the first line of the principal series are obtainable. Selényi[3] found that the threshold of a composite thin film of nickel and sodium on a thick layer of sodium spontaneously moved towards longer wave-lengths and then returned as the surface grew older. The maximum wave-length was much beyond that of the first line of the principal series. In these experiments, unlike those of Ives and Olpin, the thickness of the film was not deliberately controlled, but this does not preclude a spontaneous alteration in the thickness. Returning to the experiments of Ives and Johnsrud, it is interesting to consider how the stage of maximum threshold shift is related to the other phenomena of thin films. There is indirect evidence in Ives' 1924 work[4] that the maximum excursion of the threshold coincides with the maximum photoelectric current, both of which occur with less alkali metal than is necessary to develop the maximum polarization selectivity. This, in turn, occurs with less alkali metal than that corresponding to equilibrium thickness of the film deposited spontaneously at room temperature. Referring to Fig. 5-11, the maximum threshold shift would be closer to the

[1] N. R. Campbell, *Phil. Mag.*, **8**, 667 (1929).

[2] A. R. Olpin, *Phys. Rev.*, **36**, 251 (1930).

[3] Similar results have been obtained by Selényi for Na treated with O_2, although the gain in sensitivity is apparently considerably less than in Olpin's work. (Selényi, "Photoelectric Cells and Their Applications," p. 25; *cf.* footnote 1, p. 171.)

[4] H. E. Ives, *Astrophys. Jour.*, **60**, 209 (1924).

maximum of the $I\|$ and $I\perp$ curves individually than to the maximum of the $I\|/I\perp$ ratio. The results of Suhrmann and Theissing[1] (Fig. 5-12), however, indicate that the maxima in the $I\|$ and $I\perp$ curves occur at about the same stage as the maximum in the $I\|/I\perp$ ratio, and that this is a later stage than that corresponding to the greatest threshold shift.[2]

5-13. Emission Velocities and Polarization Selectivity.—The remarkable way in which the $I\|$ current can be made to change relative to the $I\perp$ current suggests that they originate in very different ways. This has led investigators to examine whether or not any difference can be found in their emission velocities. Up to the present not the slightest difference has been found.

The *maximum* emission velocity of electrons is the same, according to Elster and Geitel,[3] when monochromatic light is used, whether the electrons are produced by $E\|$ or by $E\perp$ light, even though there is strong polarization selectivity ($I\| \gg I\perp$). Wolf,[4] and Ives, Olpin and Johnsrud,[5] find that the *distribution* of velocities between zero and the maximum velocity is the same for both cases, in addition to the agreement for the maximum emission velocities. (It is true that Wolf found a consistent tendency for the $E\|$ electrons to exceed the corresponding $E\perp$ electrons by a few hundredths of a volt, but on the other hand this amount is within the error of experiment as estimated by him.) Wolf's method—the magnetic deflection method originated by Ramsauer—is better adapted for a precise study of the most probable emission velocities than of the maximum emission velocities. He found that his results could be represented accurately by $(\frac{1}{2})mv^2 = k\nu - p$, where k, instead of h, is appropriate to most probable velocities. Finally, the verification of Einstein's equation for the relation between the maximum emission velocity and the frequency appears to be totally unaffected by the presence or absence of strong selectivity, and by the fact that some velocities may be measured within the wave-length region of strong selectivity and others almost outside it (Millikan[6] and Teichmann[7]). Moreover, the agreement between the values of h calculated from experiments on metals (Li and Na) showing strong selectivity (Millikan[6]) and those obtained with metals (Al, Zn, Sn, Ni, etc.) showing no selectivity (Lukirsky and Prile-

[1] R. Suhrmann and H. Theissing, *Zeits. f. Phys.*, **55**, 707 (1929).

[2] By means of a device similar to that suggested in Sec. **5-4**, p. 155, Brady (*Phys. Rev.*, **37**, 230 [1931]) could estimate the thickness of a film of K as it formed on a metal surface. He found that the greatest threshold shift towards the red took place when the film was approximately one atomic layer thick, while the maximum emission occurred for a thickness of five atomic layers. The surface had the characteristics of K in bulk when the thickness exceeded twelve atomic layers.

[3] J. Elster and H. Geitel, *Phys. Zeits.*, **10**, 457 (1909).

[4] F. Wolf, *Ann. d. Phys.*, **83**, 1000 (1927). See also Sec. **4-6**.

[5] H. E. Ives, A. R. Olpin, and A. L. Johnsrud, *Phys. Rev.*, **32**, 57 (1928).

[6] R. A. Millikan, *Phys. Rev.*, **7**, 355 (1916).

[7] H. Teichmann, *Ann. d. Phys.*, **1**, 1069 (1929).

zaev[1]) indicates that neither spectral nor polarization selectivity has any influence on emission velocities.

The foregoing discussion is concerned with materials which show polarization selectivity when in "thick layers." Strong polarization selectivity is also obtained with "thin films" of alkali metals on some supporting metal. No one seems to have investigated the distribution of velocities in these cases. In view of Lukirsky and Prilezaev's discovery[1] that the distribution of velocities of photoelectrons from sputtered films of platinum depends considerably on the thickness of the film, it would be of considerable interest to extend the investigation to thin films of alkali metals.

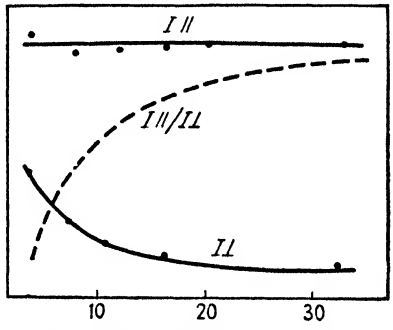

FIG. 5-30.—Change in $I\|$ and $I\perp$ currents as the Na-K alloy cools down to room temperature. Abscissa, time in min.

5-14. Polarization Selectivity and Temperature.—Very little is known about the effect of temperature on the polarization selectivity of the alkali metals. The results of Ives[2] and of Ives and Johnsrud[3] (considered in Chapter III) on the change of the photoelectric current with temperature have no direct bearing, since unpolarized light was used. In another investigation,[4] Ives and Johnsrud found that the ratio $I\|/I\perp$ increased as the temperature of the Na-K alloy fell from a temperature high enough to produce visible distillation (150°C ?) to room temperature. The change in the ratio was entirely due to a diminution in the $I\perp$ current (Fig. 5-30). These results were confirmed by Quarder in an unpublished research, according to Gudden.[5] Gudden suggests that perhaps the increase in $I\perp$ with temperature is due to an increase in the disorientation of the surface due to molecular heat motion, allowing the $I\perp$ electrons to escape more readily. It would be interesting to extend these investigations to higher and lower temperatures.

5-15. Discussion.—A consideration of the results discussed in previous sections suggests that pronounced polarization selectivity is always associated with spectral selectivity. It is true that Ives did not find any spectral selectivity for thin films of alkali metals on clean supporting metals showing strong polarization selectivity within the spectral range of his experiments. But the discovery of spectral selectivity farther in the ultra-violet, by Suhrmann and Theissing, for a

[1] P. LUKIRSKY and S. PRILEZAEV, *Zeits. f. Phys.*, **49**, 236 (1928).
[2] H. E. IVES, *Jour. Opt. Soc. Amer.*, **8**, 551 (1924).
[3] H. E. IVES and A. L. JOHNSRUD, *Jour. Opt. Soc. Amer.*, **11**, 565 (1925).
[4] H. E. IVES and A. L. JOHNSRUD, *Astrophys. Jour.*, **60**, 232 (1924).
[5] B. GUDDEN, "Lichtelektrische Erscheinungen," p. 102 (Julius Springer, 1928).

thin film of K on Pt, makes it probable that all thin films of alkali metals on clean metallic supporting surfaces have spectral selectivity.[1] Spectral selectivity has been observed for a great many surfaces in which it is impossible to test for polarization selectivity, because the surfaces are not optically flat. It seems probable that, if suitable surfaces could be obtained for testing, a strong maximum in the spectral selectivity curve (plotted in terms of absorbed light) would be found to be accompanied by polarization selectivity. There is no theoretical necessity for this correlation; it usually happens to be the case experimentally.

As a general rule the selective maxima of the various materials occur at wave-lengths in the same sequence as that of their respective thresholds. It is also noteworthy that the wave-length of the selective maximum is generally of the order of two-thirds that of the threshold, a result predicted by Richardson's theory (Sec. **6-10**), a theory, be it noted, which takes no account of the state of polarization of the light.

Polarization selectivity—the large ratio of $I\|/I\perp$—suggests that the photoelectrons tend to follow the direction of the electric vector, an effect perhaps to be expected on the classical theory of radiation. But it is difficult to see why this effect should be restricted to some surfaces and then within a limited range of wave-lengths. We know from the work of Bubb and others that X-ray photoelectrons are ejected initially from the atom, mainly in the direction of the electric vector. The comprehensive investigation of Ives, Olpin, and Johnsrud (Sec. **4-7**) shows that the photoelectrons tend to follow the direction of the electric vector when this is perpendicular to the surface. However, the concentration of electrons within a cone of, say, 10 deg around the normal is only about 10 to 20 per cent greater for the $E\|$ case than for the $E\perp$ case, even when $I\|$ is about twenty times greater than $I\perp$. If, as Lawrence and Chaffee have shown,[2] the photoelectrons start off initially in the direction of the electric vector, evidently some effect, presumably collisions, almost completely obliterates the tendency to follow this direction. But this makes it somewhat difficult to believe that the explanation contemplated is adequate to account for the enormous ratios of $I\|/I\perp$ frequently observed.

The identity of the maximum velocities and also of the velocity distributions of photoelectrons excited by $E\|$ and $E\perp$ light, is an obstacle to any theory which attempts to attribute the $I\|$ and $I\perp$ currents to different origins. On the assumption that the initial direction of motion

[1] Note: This statement must not be interpreted too literally, for, in the work referred to, the polarization selectivity becomes evident a little earlier than the spectral selectivity in the course of the building up of the film.

[2] E. O. Lawrence and M. A. Chaffee, *Phys. Rev.*, **36**, 1099 (1930); discussion in Sec. **7-14**, p. 283.

of a photoelectron is that of the electric vector, it is easy to see that, if the light penetrates deeply into the metal and evokes photoelectrons at all levels, the number of electrons emerging from the surface will be the same for $E\|$ and $E\perp$ because all sense of original direction of motion is obliterated after a few collisions. Neither should there be any distinction between the maximum emission velocities and the distributions of velocities. But, to consider the other extreme, if all the light were absorbed in a single surface layer of atoms, we should expect to find $I\|$ to be greater than $I\perp$, and to find the electron paths concentrated around the normal to the surface. The maximum emission velocities would be the same if, in the $E\perp$ case, we assume that some at least of the photoelectrons escape after an elastic collision. We should expect perhaps a difference in the distributions of velocities; the reason why no difference is obtained experimentally, even for a metal showing strong polarization selectivity, is that the blurring of the initial direction of motion is nearly complete.

We have stated that there are reasons for believing that the greatest photoelectric currents and the maximum spectral and polarization selectivities for thin films occur when there is only enough alkali metal on the surface to form a single layer of atoms, perhaps not even closely packed. With such films, Suhrmann and Theissing have obtained photoelectric currents as large as 5.6×10^{-2} coul/cal, from which we infer a yield of one electron for 14 quanta.[1] All the indirect evidence that we possess as to the penetration of light into metals suggests that the light is not completely absorbed until it has passed through perhaps a hundred atomic layers. Consequently in the experiments of Suhrmann and Theissing we are getting many *more* electrons than can be accounted for by the quanta actually absorbed by the alkali atoms, and hence we must suppose that the electrons come mainly from the supporting metal, the function of the few sparsely distributed alkali-metal atoms being to lower the work function of the surface as a whole.[2]

Ives' discovery that a monatomic layer of rubidium on glass gave as large a photoelectric current as a similar layer on platinum might be cited as evidence for the view that all the photoelectric current comes from the alkali metal. However, even an insulator is photoelectrically sensitive in the far ultra-violet, and an alkali film on it no doubt reduces

[1] Note: On the assumption that the electrons follow the electric vector and that half of them are directed inwards and therefore do not emerge, the yield, now reckoned for those with a possibility of emerging, rises to one electron per seven quanta.

[2] The absorption coefficient of mercury vapor for its own resonance radiation implies that, for this particular radiation, a mercury atom can, on the average, absorb all the radiation falling upon an area ten times that of its own cross-sectional area. We have not the slightest evidence for believing that isolated alkali-metal atoms on a supporting metal have any such property, but if they had, the argument in the text would be invalidated.

its work function. It would be difficult, however, to account for the high yield in view of the great depth of penetration of light into the glass combined with the presumably small electronic mean free path. Further conjecture is superfluous; what we need is a quantitative study of the photoelectric current from the thin film, the amount of light absorbed by it, and the amount absorbed in the glass.

In view of the difficulty of arriving at any rational explanation of the behavior of thin films of alkali metals on clean supporting metals, it is manifestly still more difficult to account for the properties of the more complicated surfaces recently investigated by Campbell, Koller, and Olpin. Campbell[1] maintains that the significant characteristic of such a surface is an electronegative gas film between the electropositive alkali-metal film and the supporting metal. To this are to be attributed, in some way, the abnormally high photoelectric currents for a certain range of wave-lengths. By postulating that such a surface may be associated with a potential variation at the surface of the type shown in Fig. 6-26 in place of the simple potential jump at a clean surface of a homogeneous metal (Fig. 6-23), Fowler[2] showed that wave mechanics led to an abnormally high transmission coefficient for photoelectrons called out by a certain range of wave-lengths. The argument applies only to those electrons starting off in a direction approximately perpendicular to the surface, hence theory predicts an abnormally large current only for the case when the electric vector has a component perpendicular to the surface—and this is what is found experimentally. Fuller details of this argument will be given in Sec. **6-29**.

Note: A most suggestive interpretation of polarization selectivity has very recently been presented by Ives (*Phys. Rev.*, **38**, 1209, 1477 [1931]). He does not attempt—as others have tried heretofore and failed—to link the photoelectric current with the amount of light *absorbed* by the illuminated metal. On the assumption that practically all the emitted photoelectrons come from a surface layer of atoms, whereas the light penetrates several hundred such layers, he considers that the photoelectrons must be accounted for in terms of the energy of the electric vibrations just *at* the surface. Here the incident, reflected, and refracted waves form a pattern of standing waves, whose intensities may be calculated by the electromagnetic theory in terms of certain optical constants, and it is possible to compute the energies at the surface associated with the component of electric force parallel to the surface, and with that perpendicular to the surface. The values obtained appear to be adequate to account for the abnormally high values of $I\|/I\perp$ ratios as well as to describe the dependence of these ratios upon angle of incidence. At present the chief obstacle to a thorough quantitative check is the absence of dependable values for the optical constants.

The notion that the selective effect may be accounted for by purely optical considerations also receives support from the recent work of Fleischmann (*Die Naturwis-*

[1] N. R. Campbell, "Photoelectric Cells and Their Applications," p. 10 (The Physical and Optical Societies of London, 1930).

[2] R. H. Fowler, *Proc. Roy. Soc.*, **128**, 123 (1930).

senschaften, **19**, 826 [1931]) who found that while certain thin films of K on glass or quartz have a selective absorption band for $E\|$ light they do not absorb $E\perp$ light at all. If it should happen that further quantitative tests demonstrate that the selective effect can be accounted for by optical considerations alone, as indicated by the work of Ives and Fleischmann, then it would appear that the explanation suggested by Campbell and Fowler (Sec. **5-15** and **6-29**) is superfluous.

CHAPTER VI

THEORIES OF PHOTOELECTRIC EMISSION

We have confined our attention hitherto to the large mass of experimental data in the field of photoelectricity, interpreting the results where possible on the basis of a more or less simple picture of the process and pointing out only the more direct theoretical implications. We come now to a more detailed discussion of the theoretical aspects of the photoelectric effect in metals.

6-1. The Einstein Equation.—It has already been pointed out[1] that the Einstein equation can be derived directly by adopting a purely corpuscular view of the nature of the photoelectric process, but that it cannot be understood on the basis of the classical wave theory. The experimental verification of this important relation therefore constitutes one of the most brilliant triumphs of, and at the same time one of the most powerful arguments for, a quantum theory of radiation. Curiously enough, however, it has recently been shown[2] that the Einstein equation *can* be derived on the basis of the wave theory of light—but only if we also adopt a wave theory of the electron! One may say, then, that the photoelectric effect, as well as its close relative the Compton effect, can be understood if both light and electrons are corpuscles, or if they are both waves, but not if one is a corpuscle while the other is a wave! It will be one of the purposes of the last part of the present chapter to present briefly the wave theory of the photoelectric effect.

6-2. Other Theoretical Problems.—The derivation of the Einstein equation, in spite of its fundamental significance, is not the only theoretical problem of importance in the domain of photoelectricity. For, as we have seen,[3] in order to describe completely the photoelectric emission from a metallic surface it is necessary to specify not only the maximum velocity of the emitted electrons, but also their number and velocity distribution as well as the way in which these factors depend on the frequency and state of polarization of the light, and the nature, state of aggregation, and temperature of the surface. A general solution of the problem would thus be exceedingly complicated, and it is probably not feasible to attempt it at the present stage of our knowledge. Nevertheless, considerable progress has been made in certain directions and any

[1] See Chap. II, p. 7.

[2] G. Wentzel, "Probleme der Modernen Physik," *Sommerfeld Festschrift*, p. 79 (S. Hirzel, 1928).

[3] See Sec. 3-1.

one working in this field will find it necessary to be familiar with the present status of the problem.

Before any attempt at a complete theoretical interpretation of photoelectric results can be made, it is necessary to consider more in detail the interaction taking place between radiation and electrons within the metal. This means that we must adopt not only a definite theory of radiation but also a theory of electrons in metals. The photoelectric problem is thus closely related to the whole problem of electron conduction, and no theory of metallic conduction can be considered complete which does not offer an adequate interpretation of the various problems related to the photoelectric effect. On the other hand, photoelectric results will act as a valuable constructive guide in the development of a more complete electron theory of matter.

It will be convenient to divide the discussion of photoelectric theories into two parts. In Part I will be taken up the important developments which have been made on the basis of the *classical* theory of electrons and its various modifications. The term "classical theory" is used rather loosely—as is customary in other branches of physics—to cover all the theories except the most recent one. In the present case this means all of the theories developed previous to 1927—in which year Pauli[1] and Sommerfeld[2] laid the foundations for an entirely new theory of electrons in metals, based on a set of postulates radically different from those of the older theories. Their theory has had conspicuous success in many directions and seems destined to play an important rôle in the future development of the field. The interpretation of the laws of photoelectricity in the light of this theory will be taken up in Part II of this chapter.

I. THE CLASSICAL THEORY

6-3. Basis of the Classical Theory.—The classical theory of metallic conduction in its original form, as developed by Riecke,[3] Drude,[4] Lorentz,[5] and others,[6] makes two fundamental assumptions. In the first place it is assumed that within any block of metal is to be found a swarm of free electrons which are responsible for its electrical and thermal properties. These electrons are *free* in the sense that they are not permanently bound

[1] W. Pauli, *Zeits. f. Phys.*, **41**, 81 (1927).

[2] A. Sommerfeld, *Zeits. f. Phys.*, **47**, 1 (1928).

[3] E. Riecke, *Ann. d. Phys.*, **2**, 835 (1900).

[4] P. Drude, *Ann. d. Phys.*, **1**, 566 (1900).

[5] H. A. Lorentz, "Theory of Electrons" (Teubner, 1915); O. W. Richardson, "Electron Theory of Matter" (Cambridge University Press, 1916).

[6] Excellent reviews of the classical electron theory have been given by K. K. Darrow, *Bell Syst. Tech. Jour.*, **3**, 621 (1924); E. Kretschmann, *Phys. Zeits.*, **28**, 565 (1927); E. Grüneisen, *Handbuch der Experimentalphysik*, Vol. XIII, p. 64 (1928).

to atomic systems but may wander at random in the spaces between atomic centers. In the second place it is assumed that these electrons, through collisions with the atoms, acquire thermal energies which are on the average just equal to the average kinetic energy of the atoms (*equipartition*), and which have a Maxwellian distribution about this average value. Thus at temperature T the average thermal energy of a single electron is $\frac{3}{2}kT$, where k is the Boltzmann constant. In the process of *electrical conduction*, then, it is imagined that the applied electric field superimposes on the random thermal velocities of the electrons a small drift in the direction of the field. The process of *thermal conduction* is assumed to be due to the transfer of energy from electrons in the regions of high temperatures and large thermal energies, to electrons of smaller kinetic energy in the cooler portions of the metal. The ratio between the electrical and thermal conductivities —the Wiedemann-Franz ratio—comes out to be a constant whose numerical value is very close to the value obtained from experiment. This was the chief triumph of the classical theory, but not its only one. It was used successfully by Lorentz[1] to derive the Rayleigh-Jeans radiation law and by Richardson[2] to derive the well-known equation of thermionic emission. The theory was found to give a qualitative picture of the various thermoelectric effects, but here it failed badly by giving numerical results which were not even of the right order of magnitude.[3]

6-4. The Specific-heat Difficulty.—A serious difficulty confronted the classical theory at the outset, one which has an important bearing on the problems of photoelectric and thermionic emission. It is well known that the specific heat of a metal may be accurately calculated by considering only the thermal energies of the atoms, neglecting that of the electrons. Now there are a number of lines of evidence which indicate that the number of free electrons per unit volume must be of the same order of magnitude as the number of atoms. Hence if each electron is assigned the energy $\frac{3}{2}kT$, the calculated value of the specific heat is 50 per cent greater than the observed.[4] If we assume that the electrons after all do *not* have thermal energies, the specific-heat difficulty is removed, but we obtain wrong values for the thermal and electrical conductivities. The only way out seems to be to assume that electron energies are not zero but are independent of the temperature, and this is the postulate which has been employed in the more modern theories, and which seems to be supported by experiment.

[1] H. A. Lorentz, "Theory of Electrons," pp. 69–97.
[2] O. W. Richardson, "Emission of Electricity from Hot Bodies," p. 35 (2d ed.).
[3] See O. W. Richardson, "Electron Theory of Matter," Chap. XVIII.
[4] The total energy (kinetic and potential) of an *atom* in a solid is $3kT$.

The specific-heat difficulty has been avoided in slightly different ways by recent modifications of the classical theory. For example, Frenkel[1] assumes that the electric currents are carried by bound electrons[2] which are passed from one atomic system to another. Their energies depend only on forces within the atoms, and are therefore independent of temperature. Hall[3] has proposed that both free and bound electrons partake in the various electrical and thermal processes, the number of free electrons required being sufficiently small to avoid the specific-heat difficulty. In J. J. Thomson's theory[4] the electrons are assumed to move in chains, with possibly as many as 10^4 electrons in each chain. Each of these groups as a whole takes on the equipartition value of the kinetic energy, so the total contribution of the electrons to the specific heat of the metal becomes negligible. A similar idea has also been employed by Bridgman.[5]

6-5. The Temperature Variation of the Photoelectric Effect.—This question is obviously closely related to the question of electron energies in metals. As we have seen in Chapter III, it has been well established by experiment that under ordinary conditions the photoelectric effect is nearly independent of temperature, although there are exceptions in the case of the alkali metals at low temperatures and the more refractory metals at very high temperatures. Now, on the basis of *any* theory, the energy with which a photoelectron will emerge from a metal surface must be equal to the amount $h\nu$ which it absorbs from the incident light, plus the kinetic energy E_k which it previously possessed within the metal, minus the energy ϕe which it loses in penetrating the surface. That is

$$\tfrac{1}{2}mv_{\max}^2 = h\nu + E_k - \phi e. \tag{6-1}$$

Thus the least frequency which will cause an electron to emerge with zero velocity will be given by

$$h\nu_0 = \phi e - E_k.$$

The variation of this threshold frequency with temperature then will be

$$\frac{d(h\nu_0)}{dT} = e\frac{d\phi}{dT} - \frac{dE_k}{dT}. \tag{6-2}$$

Thus a shift in the photoelectric threshold with temperature may be due to either a change in E_k or a change in ϕ. These two effects will probably be indistinguishable experimentally, although they will have

[1] J. Frenkel, *Zeits. f. Phys.*, **29**, 214 (1924).

[2] K. Højendahl, *Phil. Mag.*, **48**, 349 (1924); P. W. Bridgman, *Phys. Rev.*, **17**, 161 (1921); *Solvay Congress Report* (1924); H. M. Barlow, *Phil. Mag.*, **8**, 289 (1929). These authors also discuss theories of conduction by bound electrons.

[3] E. H. Hall, *Phys. Rev.*, **28**, 392 (1926).

[4] J. J. Thomson, *Phil. Mag.*, **44**, 657 (1922).

[5] P. W. Bridgman, *Phys. Rev.*, **19**, 114 (1922).

different theoretical consequences. Leaving aside for the moment any change in ϕ we would have on the classical theory $E_k = \frac{3}{2}kT$,[1] and hence,

$$\frac{d(h\nu_0)}{dT} = -\tfrac{3}{2}k.$$

This amounts to a change in the work function of the surface of approximately 1.29×10^{-4} volt/deg, which is less than the smallest change that could be detected in many of the experiments which have been reported. Nevertheless, Millikan and Winchester[2] found that for 11 different metals the change in photoelectric current with temperature was considerably less than would be expected on the basis of the classical theory. In many of the later experiments,[3] a temperature effect as large as that predicted by the classical theory would probably have been observed, so that it is usually assumed that the theory is *not* in agreement with most experiments.[4] Until recent years, however, this was not interpreted as a contradiction to the theory but was taken as evidence that the photoelectrons were not initially free but were bound to atomic systems. A discussion of this possibility will be given in Sec. **6-7**. Recently, however, there has been an accumulation of evidence[5] pointing to the fact that even for free electrons dE_k/dT is nearly zero and hence no temperature variation of the photoelectric effect is to be expected (see, however, Sec. **6-30**).

Nielsen[6] came to the conclusion that on the basis of the classical theory $d(h\nu_0)/dT = 0$, except for terms of the order of the Thomson coefficient. In his definition of the photoelectric work function, however, he included a term $-\frac{3}{2}kT$, the energy of the electrons in thermal equilibrium *outside* the metal. It is doubtful if this term can be included in the work function as ordinarily measured.

It has been suggested that, even though it seems necessary to assume $dE_k/dT = 0$ at ordinary temperatures, it may become positive at high temperatures. Lewis, Eastman, and Young[7] have used this assumption to explain the rise in metallic specific heats at high temperatures. Millikan and Eyring[8] also found that in pulling electrons

[1] Actually this is not quite correct, since E_k is the *maximum* kinetic energy possessed by the electrons within the metal, while $\frac{3}{2}kT$ represents the *average* energy. Because of the assumed Maxwell distribution there will be no maximum energy, which means that the maximum energy of emission and, hence, the threshold will not be sharply defined except at the absolute zero. Since, however, the maximum energy and the threshold are obtained by extrapolation of the observed curves, the above calculations will give the order of magnitude of the expected shift of these curves, which will not be much affected by the presence of a few electrons of energy higher than $\frac{3}{2}kT$.

[2] R. A. Millikan and G. Winchester, *Phil. Mag.*, **14**, 188 (1907).

[3] O. Koppius, *Phys. Rev.*, **18**, 443 (1921); J. R. Nielsen, *Phys. Rev.*, **25**, 30 (1925). See also Sec. **3-26**.

[4] See, however, the still more recent experiments described in Sec. **3-28**.

[5] C. Davisson and L. H. Germer, *Phys. Rev.*, **20**, 300 (1922).

[6] J. R. Nielsen, *Phys. Rev.*, **25**, 30 (1925).

[7] E. D. Eastman, A. M. Williams, and T. F. Young, *Jour. Am. Chem. Soc.*, **46**, 1184 (1924).

[8] R. A. Millikan and C. F. Eyring, *Phys. Rev.*, **27**, 51 (1926).

from metals by intense electric fields, the field currents were independent of temperature at ordinary temperatures, but showed an increase above about 1100°K.[1] They attributed this to an increase in electron energies at high temperatures. Such an effect might also explain the increase in the photoelectric emission from metals observed at high temperatures.

It will be seen that the conditions that $dE_k/dT = 0$ at ordinary temperatures and is positive at high temperatures have been brought into the classical electron theory of metals as *ad hoc* assumptions, introduced for the purpose of explaining certain electronic phenomena. On the other hand, they come out as a natural result of the Sommerfeld electron theory, and thus account for much of its success.

6-6. The Temperature Variation of ϕ.—We have neglected the possibility of a variation with temperature of ϕ, the work function of the surface. Experiments show only that the difference $(\phi e - E_k)$ must be nearly constant at ordinary temperatures. Hence if E_k is independent of temperature, ϕ must be also. It has been recognized, however, that this is probably true only to a first approximation and a number of attempts have been made to deduce theoretically an accurate expression for the temperature dependence of this quantity. According to Schottky[2] the work function of a surface should be inversely proportional to the distance between atoms; hence, due to thermal expansion, the work function should decrease with rising temperatures. More detailed calculations on the basis of thermodynamics have been made by Bridgman[3] and Herzfeld.[4] Herzfeld found that the photoelectric work function should be given by an expression of the form,

$$\phi = q_1 - q_2\int_0^T \beta dT, \tag{6-3}$$

where q_1 and q_2 are constants and β is the coefficient of volume expansion of the metal. He computed numerically the order of magnitude of the change to be expected in ϕ for a temperature change of 100°C, obtaining the following results, expressed in millivolts:

K	Al	Mg	Zn	Cu	Ag	Au	Fe	Ni	Pt	Pb	Sb
125	36	39	43	25	29	21	17	23	15	43	18

The values are for the most part too small to be detected experimentally. However, they are of the right order of magnitude to account for the results of Ives[5] for K at low temperatures and the results of DuBridge[6] on Pt at high temperatures.

The question of the temperature variation of ϕ is closely related to that of the variations of the constant A in the Richardson thermionic equation, and hence will be discussed again in Sec. **6-14.**

[1] N. A. DE BRUYNE, *Phys. Rev.*, **35**, 172 (1930), finds the field currents independent of temperature even at high temperatures.

[2] W. SCHOTTKY, *Zeits. f. Phys.*, **14**, 63 (1923); see also Sec. **6-15.**

[3] P. W. BRIDGMAN, *Phys. Rev.*, **31**, 90 (1925); **31**, 862 (1925).

[4] K. F. HERZFELD, *Phys. Rev.*, **35**, 248 (1930).

[5] H. E. IVES, *Jour. Opt. Soc. Amer.*, **8**, 551 (1924).

[6] L. A. DUBRIDGE, *Phys. Rev.*, **29**, 451 (1927).

6-7. Are the Photoelectrons Initially Free or Bound?—The question as to the origin of the photoelectrons has played a prominent part in the development of photoelectric theories, and unless a definite answer can be found it will be difficult to develop a definite picture of the complete photoelectric process.

The most natural assumption seems to be that the electrons are initially *free*, because the elements which are most photoelectrically active are just the ones which contain large numbers of free electrons, namely the metals. It was thought at one time that the independence of the photoelectric effect of temperature was convincing evidence that the photoelectrons, since they did not partake in thermal agitation, must be initially *bound* to atomic systems. Obviously, however, this argument depended on the validity of the classical electron-gas theory of metals which has more recently been seriously discredited if not completely overthrown—at least in regard to the assumption of equipartition.

The question was treated in some detail by Millikan[1] in connection with his measurements of stopping potentials. His analysis was briefly as follows: Consider a metal plate illuminated by light of frequency ν discharging photoelectrons into a surrounding collecting cylinder whose potential relative to the plate is V_0. V_0 includes the applied potential V and the contact potential K. Then, if V is adjusted until there is no flow of electrons between plate and cylinder, we have from the Einstein equation,

$$(V + K)e = h\nu - \phi e. \tag{6-4}$$

Suppose that ϕ is composed of two parts; ϕ_1, the work necessary to extract the electron from the parent atom; and ϕ_2, the energy lost in penetrating the surface. Then

$$(V + K)e = h\nu - (\phi_1 + \phi_2)e. \tag{6-5}$$

If we now substitute a second metal for the first and denote the corresponding quantities for this metal by primed letters, we may write

$$(V' + K')e = h\nu - (\phi_1' + \phi_2')e. \tag{6-6}$$

Subtracting Eq. (6-5) from (6-6), we have

$$(V' - V) + (K' - K) = (\phi_1 - \phi_1') + (\phi_2 - \phi_2'). \tag{6-7}$$

Now the stopping potential experiments show clearly that in all cases $V' - V = 0$ and, since the contact difference of potential between two

[1] R. A. Millikan, *Phys. Rev.*, 7, 355 (1916).

metals is simply equal to the difference between their surface potential jumps, *i.e.*, $K' - K = \phi_2 - \phi_2'$ therefore,[1]

$$\phi_1 - \phi_1' = 0.$$

Hence the energy required to release the electrons from the parent atom is either zero or the same for all metals. The latter alternative is inconsistent with well-established views of atomic structure, and hence we are led to conclude that the photoelectrons were initially free. It must be remarked, however, that this argument applies strictly only to the electrons which emerge from the metal with the maximum velocity given by the Einstein equation, since the stopping potential experiments deal only with these. There still exists the possibility that the great mass of electrons which emerge with velocities less than the maximum were initially bound.

6-8. The Compton Effect.—New evidence of a convincing kind was introduced into the problem through the discovery and interpretation of the Compton[2] effect. Compton's experiments showed clearly that in elementary processes between electrons and quanta, both energy and momentum are conserved. Now it is impossible for a *free* electron to absorb the entire energy of an impinging quantum. For then we should have from the conservation of energy,

$$h\nu = \tfrac{1}{2}mv^2,$$

and from conservation of momentum,

$$\frac{h\nu}{c} = mv.$$

And this leads to the impossible result that $v = 2c$, v being the velocity of the electron, and c the velocity of light.[3] Hence a third body must take part in the collision. This third body may be either an atom, or other parent system to which the electron is bound, or it may be a scattered quantum. In the first case, it *will* be possible for the electron to absorb nearly all the energy of the incident quantum and we would then have a photoelectric effect. In the second case, we have the Compton effect in which the electron receives only a small fraction of the energy $h\nu$, the rest appearing as the energy $h\nu'$ of the scattered quantum.[4]

Since in the photoelectric effect the electrons do absorb practically the entire energy $h\nu$ it is evident they could not have been initially free.

[1] It should be pointed out that in a theory in which the conduction electrons are assumed to be bound, we have, instead of this relation, simply $K' - K = \phi' - \phi$ and hence no conclusions as to the values of ϕ_1 or ϕ_2 may be drawn.

[2] A. H. Compton, *Phys. Rev.*, **21**, 483 and 715 (1923); see also "X-rays and Electrons," p. 260 (D. Van Nostrand Company, Inc., 1926).

[3] Making use of the relativity expressions for the energy and momentum, we obtain instead the equally impossible result, $v = c$.

[4] See Sec. 11-10 for a further discussion of the theory of the Compton effect.

Why is it then that appreciable photoelectric effects are observed only with the metals which have a copious supply of free electrons?

A number of solutions of this difficulty have been proposed. Mendenhall,[1] Epstein,[2] and Wolff[3] have suggested that the free electrons may acquire the energy of the quanta through a *double* process, since the single one is forbidden by the Compton equations. The first step would be an absorption of the energy by an *atom* with which the quantum makes an inelastic collision, raising the atom to an excited state. The second step would be the transfer of this energy to a free electron through a "collision of the second kind."[4] It is not impossible that such collisions may occur in the solid as well as in the vapor state. In line with this suggestion Ives and Olpin[5] have recently found striking evidence that, in some cases at least, the atoms do play an important rôle in the photoelectric emission process. They have found that for films of the alkali metals of a certain critical thickness the photoelectric threshold coincides accurately with the first resonance potential of the atom. This means that frequencies sufficiently large to excite (without ionizing) an individual atom can produce a photoelectric emission. Possibly the energy of excitation is given over to free electrons through collisions.

A second way out of the difficulty has been made use of by Wentzel.[6] He points out that a free electron can absorb the energy $h\nu$ without violating the principles of conservation of energy and momentum *if the incident wave train is damped.* This follows from the fact that a damped wave can no longer be considered as monochromatic, but may be resolved into Fourier components, each having the same frequency ν but different wave-lengths λ. Now the energy of each component is $h\nu$, while its momentum is h/λ. Since $\nu\lambda$ is no longer equal to c, the electron may absorb the energy $h\nu$ and momentum h/λ without having to attain a velocity greater than c. Since an incident light wave on entering a metal is strongly damped, a photoelectric process with the free electrons is made possible. This point of view, however, is open to the objection pointed out by Tamm and Schubin[7] that the photoelectric effect itself causes a large part of the damping of the incident wave train in the metal, and hence a damped wave train cannot be used to explain the photoelectric effect!

[1] C. E. Mendenhall, *Science*, **59**, 229 (1924).

[2] P. S. Epstein, quoted by R. A. Millikan, "The Electron," p. 256 (The University of Chicago Press, 1924).

[3] H. T. Wolff, *Zeits. f. Phys.*, **52**, 158 (1928).

[4] For a discussion of such collisions see, for example, A. E. Ruark and H. C. Urey, "Atoms, Molecules and Quanta," p. 75 (McGraw-Hill Book Company, Inc., 1930).

[5] H. E. Ives and A. R. Olpin, *Phys. Rev.*, **34**, 117 (1929). See Sec. **5-12** for a more complete discussion of these experiments.

[6] G. Wentzel, "Probleme der Modernen Physik," p. 79.

[7] I. Tamm and S. Schubin, *Zeits. f. Phys.*, **68**, 97 (1931).

Still another alternative—and apparently the most satisfactory—is to consider that the metal block itself acts as the parent system to which the electrons are bound and which acts as the third body in the collision. This solution of the difficulty seems to be the one most generally accepted. Tamm and Schubin have quite recently pointed out, however, that, if this is the case, then at the instant of interaction the electrons which absorb the energy $h\nu$ must actually be in the force field which binds them to the metal, *i.e.*, the surface field which gives rise to the work function. But this field exists only at the surface of the metal, and in fact a large part of it is apparently outside the surface! Now there should be an atmosphere of electrons just outside the metal surface, composed of those electrons which have come up to the surface, but which are being turned back because they lack the energy to escape through the surface field. On the basis of the wave mechanics, the density of electrons in this region can be computed. According to Tamm and Schubin it is these electrons which account for the greater part of the photoelectric emission from metals. On this basis they have developed a theory, to be discussed in Sec. **6-26**, which actually gives quantitatively correct values for the photoelectric yield and its dependence on the incident frequency.[1]

6-9. The Spectral Distribution Function.—In the analysis given at the beginning of Chapter III it was shown that the photoelectric emission from a surface could be completely specified if the velocity distribution function $\Psi(\nu, v)$ and the spectral distribution function $F(\nu)$ were known. The general forms of these functions for various metals have been obtained empirically, but it would be highly desirable to have an exact mathematical expression for them derived directly from theory. In view of the extreme complexity of the problem and of the weakness of the simple classical electron-gas theory it is not surprising that no satisfactory solution has been obtained—in fact no attempt seems to have been made to derive an exact expression for $\Psi(\nu, v)$.[2] The function $F(\nu)$, which is actually of more practical importance, has received more attention, and Richardson,[3] Uspensky,[4] and J. J. Thomson[5] have derived expressions which do not agree with each other, but which have certain features that agree with experiment. All three of these theories will be outlined briefly, not so much because of the importance of the results obtained, but because they give some insight into the possible mechanism of the photoelectric process.

[1] However this theory has recently been severely criticized as being quantitatively incorrect in certain respects by J. Frenkel, *Phys. Rev.* **38**, 309 (1931).

[2] See, however, A. Becker, *Handbuch der Experimentalphysik*, Vol. XXIII, 1258 (1928).

[3] O. W. Richardson, "Electron Theory of Matter," p. 469.

[4] W. Uspensky, *Zeits. f. Phys.*, **40**, 456 (1926).

[5] J. J. Thomson, *Phil. Mag.*, **2**, 674 (1926).

6-10. Richardson's Theory.—Consider a constant temperature enclosure in which we have an electron vapor in equilibrium with a solid metal. If we can determine the pressure of the electron vapor when equilibrium is established, we can then calculate the number of electrons leaving the surface per unit time, and hence the emission current. From the viewpoint of thermodynamics, the evaporation of electrons can be considered in the same manner as the evaporation of a monatomic gas. We make use of the Clausius-Clapeyron equation,

$$\frac{d(\log p)}{dT} = \frac{L}{RT^2}, \tag{6-8}$$

where p is the vapor pressure, T the absolute temperature, R the gas constant, and L the heat of evaporation at constant pressure. In order to integrate to obtain p it is necessary to know the way in which L varies with T. But we know from thermodynamics that the rate of change of the heat of evaporation with temperature is equal to the difference in specific heats of the two phases at that temperature. Hence,

$$L = L_0 + \int_0^T C_p dT - \int_0^T c_p dT, \tag{6-9}$$

where C_p is the specific heat at constant pressure of the electrons in the vapor state, and c_p their specific heat in the solid. L_0 is the constant of integration and is obviously the heat of evaporation at $T = 0$. Now C_p, for a monatomic vapor, is $\frac{5}{2}R$ when referred to one mol, and if we followed the simple classical electron theory we would set the specific heat within the metal equal to $\frac{3}{2}R$. Following more modern practice, however, we set $c_p = 0$. Then $L = L_0 + \frac{5}{2}RT$ and integration of Eq. (6-8) gives

$$\log p = -\frac{L_0}{RT} + \frac{5}{2}\log T + \log A'$$

or,

$$p = A'T^{\frac{5}{2}}\epsilon^{-\frac{L_0}{RT}} \tag{6-10}$$

where A' is a constant.

Now from the kinetic theory the number of electrons striking unit area of the metal surface per unit time is

$$n = \frac{p}{(2\pi mkT)^{\frac{1}{2}}}.$$

Hence the *current* to unit area of the surface will be

$$\begin{aligned} I = ne &= AT^2\epsilon^{-\frac{L_0}{RT}} \\ &= AT^2\epsilon^{-\frac{b_0}{T}}, \end{aligned} \tag{6-11}$$

where

$$A = \frac{A'e}{(2\pi mk)^{\frac{1}{2}}} \text{ and } b_0 = \frac{L_0}{R}.$$

For equilibrium the number of electrons striking the surface must be equal to the number leaving if we neglect the number reflected. Equation (6-11) therefore gives the number of electrons leaving the surface per second. The equation will be recognized as the ordinary Richardson T^2 law of thermionic emission.[1] (We would have obtained the $T^{\frac{3}{2}}$ law had we set c_p equal to $\frac{3}{2}R$ instead of to zero.) The fact that it is accurately satisfied by thermionic measurements[2] is a check on the validity of the argument. However, no mention has been made in the analysis of the mechanism by which the electrons are to be liberated from the surface—hence the above equation must hold, whatever the mechanism, providing equilibrium conditions are approximated. Now the electrons instead of being ejected by the thermionic process alone can also be ejected photoelectrically by the action of the temperature radiation in the cavity. We conclude, therefore, that if a metal surface is illuminated by the equilibrium ("black-body") radiation corresponding to a temperature T, the number of electrons ejected must be given by Eq. (6-11).

As we have seen in Chapter III, this equation has been tested in photoelectric emission by many observers, most recently by Roy[3] and Suhrmann,[4] and found to hold in all cases. Hence it may confidently be used in the further development of the theory.

The total photoelectric emission from a metal illuminated by black-body radiation can also be calculated if the spectral distribution function $F(\nu)$ is known. It would be simply,

$$I = \frac{c}{4}\int_0^\infty F(\nu)\alpha E(\nu,T)d\nu, \tag{6-12}$$

where $E(\nu,T)$ is the black-body distribution function (of Wien or Planck),[5] α is the absorption coefficient of the metal surface for the frequency ν, so that $(c\alpha/4)Ed\nu$ is the energy in the frequency range $d\nu$ absorbed by unit area of the surface in unit time. For equilibrium conditions this value of I must be the same as that given by Eq. (6-11). Hence, substituting in the Wien expression for E, we have,

[1] In its derivation we have followed S. Dushman, *Phys. Rev.*, **21**, 623 (1923).

[2] Thermionic measurements are, however, incapable of distinguishing between the T^2 and the $T^{\frac{3}{2}}$ laws.

[3] S. C. Roy, *Proc. Roy. Soc.*, **112**, 599 (1926).

[4] R. Suhrmann, *Zeits. f. Phys.*, **33**, 63 (1925).

[5] Throughout the range of wave-lengths, effective in photoelectric emission, there is no appreciable difference between the Wien and Planck laws.

$$\left(\frac{c}{4}\right)\left(\frac{8\pi}{c^3}\right)\int_0^\infty \alpha F(\nu)h\nu^3\epsilon^{-\frac{h\nu}{kT}}d\nu = AT^2\epsilon^{-\frac{b_0}{T}} \tag{6-13}$$

This is an integral equation in which everything is known except $F(\nu)$ and it can therefore be used to solve for $F(\nu)$. Unfortunately, no general solution for this equation has been found, and it is probable that there are many solutions. Richardson, however, found the following particular solution (assuming $\alpha = 1$):

$$eF_1(\nu) = 0 \text{ for } 0 < h\nu < b_0k$$

$$eF_1(\nu) = \left(\frac{A''}{\nu^2}\right)\left(1 - \frac{\nu_0}{\nu}\right) = \left(\frac{A''}{\nu^3}\right)(\nu - \nu_0) \text{ for } b_0k < h\nu < \infty, \tag{6-14}$$

where

$$A'' = \text{const} = \frac{Ah}{R}.$$

This would lead to a spectral distribution curve of the type shown in Fig. 6-1. As to be expected, the curve plunges sharply into the axis at $\nu = \nu_0$ where $h\nu_0 = b_0k$; and it passes through a maximum at $\nu = \frac{3}{2}\nu_0$.

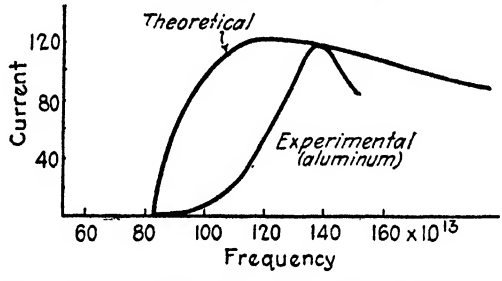

FIG. 6-1.—Theoretical spectral distribution curve (*Richardson*) compared with experimental (*Richardson and Compton*).

An experimental curve obtained by Richardson and Compton[1] for Al is also reproduced in the figure, and it is evident that its general shape does not resemble very closely that of the theoretical curve. Nevertheless, it does show a maximum at approximately the predicted position. Richardson and others[2] have obtained other curves for the alkali metals which also show such maxima, so that there is considerable experimental evidence for its existence. In many cases the maximum would lie too far in the ultra-violet to be observed.

An equation for $F(\nu)$ of exactly the same form as Richardson's Eq. (6-14) has been obtained by Lawrence,[3] who starts out with the initial assumption that thermionic

[1] O. W. RICHARDSON and K. T. COMPTON, *Phil. Mag.*, **26**, 549 (1913).

[2] O. W. RICHARDSON and A. F. A. YOUNG, *Proc. Roy. Soc.*, **107**, 377 (1925); O. W. RICHARDSON and K. T. COMPTON, *loc. cit.* See also W. H. SOUDER, *Phys. Rev.*, **8**, 327 (1916); H. E. IVES and A. L. JOHNSRUD, *Astrophys. Jour.*, **60**, 231 (1924).

[3] E. O. LAWRENCE, *Phys. Rev.*, **27**, 555 (1926).

currents from a hot body are produced by the photoelectric action of the temperature radiation within the body. Making use of the fact that the velocities of the thermionic electrons are distributed according to Maxwell's law and the energy in the radiation according to Wien's law, he is at once able to find what photoelectric spectral distribution function is necessary in order that the initial assumption be satisfied. Lawrence's derivation possesses the advantage that it does not necessitate the assumption of equilibrium conditions, but the disadvantage that his assumption that thermionic emission is due to a photoelectric process has been seriously questioned (see Sec. **6-16**). Mathematically the assumptions made by Lawrence and those made by Richardson are nearly identical.

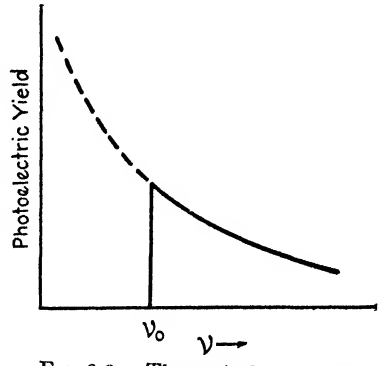

FIG. 6-2.—Theoretical spectral distribution assuming quantum equivalence.

6-11. Theory of J. J. Thomson.—It is also possible to derive an equation for the spectral distribution function by considering the *mechanics* rather than the thermodynamics of the process. This has been done by Thomson[1] and Uspensky.[2] Both of these authors suppose that every quantum of radiation absorbed by the metal confers its entire energy on a single electron which then starts off in an arbitrary direction through the metal with an initial velocity given by $\frac{1}{2}mv^2 = h\nu$. Only those can escape from the metal for which $\frac{1}{2}mv^2 > \phi e = h\nu_0$, where ϕ is the work function and ν_0 the threshold frequency. If all electrons with sufficient energy to escape actually did so, we would then have a spectral distribution curve of the form shown in Fig. 6-2. This function is zero for ν less than ν_0, while for ν greater than ν_0 it is equal to $1/h\nu$, the number of quanta per unit intensity of absorbed light. Since this "quantum equivalent" curve contains a maximum, we shall not be surprised to find one also in the final result.

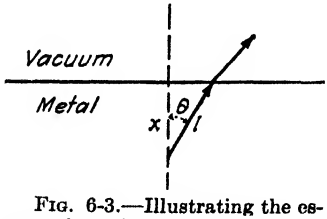

FIG. 6-3.—Illustrating the escape of an electron from a metal surface.

However, it is evident that most of the electrons receiving energy from the light will never escape from the metal. For only those can escape which actually reach the surface, after having lost some of their energy on the way, and still have a velocity whose component v_n normal to the surface is such that $\frac{1}{2}mv_n^2 > h\nu_0$. Thomson assumes that in traversing the metal, an electron starting out with an energy E will, after traversing a distance l, have the reduced energy E_l such that

$$E_l^2 = E^2 - \beta l$$

where β is a constant depending on the metal. An electron starting out at a distance

[1] J. J. THOMSON, *Phil. Mag.*, **2**, 674 (1926).
[2] W. USPENSKY, *Zeits. f. Phys.*, **40**, 456 (1926).

x from the surface in a direction making an angle θ with the normal will travel a distance $x \sec \theta$ before reaching the surface (Fig. 6-3) and will arrive with the energy $(E^2 - \beta x \sec \theta)^{\frac{1}{2}}$. The condition for escape then is

$$(E^2 - \beta x \sec \theta)^{\frac{1}{2}} \cos^2 \theta \geqq h\nu_0.$$

Now the chance that a quantum will be absorbed in the layer dx at the depth x is proportional to $\epsilon^{-\alpha x}\alpha dx$ where α is the absorption coefficient for the radiation. Hence, if the surface is illuminated by unit intensity of light, the number of quanta absorbed per second in the layer dx will be

$$\left(\frac{1}{h\nu}\right)\epsilon^{-\alpha x}\alpha dx.$$

If we assume that all directions for the initial velocity of the electron are equally probable, then the chance that this direction will lie between θ and $\theta + d\theta$ is $\frac{1}{2} \sin \theta \, d\theta$. The rate at which electrons will escape from the metal when it is illuminated by unit intensity of light of frequency ν then is

$$\left(\frac{\alpha}{2h\nu}\right)\int\int \epsilon^{-\alpha x} \sin\theta \, d\theta dx \tag{6-15}$$

The limits of integration are determined from the equation

$$(E^2 - \beta x \sec \theta)^{\frac{1}{2}} \cos^2 \theta = h\nu_0.$$

Setting $E = h\nu$, $h\nu_0/h\nu = r$ and $h^2\nu^2/\beta = d$, this equation becomes,

$$d - x \sec \theta = dr^2 \sec^4 \theta. \tag{6-16}$$

The limits for x then are from 0 to $d(1 - r^2 \sec^4 \theta) \cos \theta$ and for θ from 0 to $\cos^2 \theta = r$.

Carrying out the integration and assuming that α/β is small (*i.e.*, that the absorption coefficient for the light is much less than for the electrons) the result is,

$$F(\nu) = A\left(\frac{\alpha d}{4h\nu}\right)(1 - r)^2$$

or,

$$= A\left(\frac{\alpha h\nu}{4\beta}\right)\left[1 - \left(\frac{\nu_0}{\nu}\right)\right]^2,$$

A being a constant. Now α depends on ν and for X-rays α varies as $1/\nu^3$. Thomson assumed this variation and obtained finally,

$$F(\nu) = \left(\frac{A'}{4\beta h^2\nu^2}\right)\left(1 - \frac{\nu_0}{\nu}\right)^2. \tag{6-17}$$

However, an absorption coefficient varying inversely as the cube of the frequency is probably far from the truth for ultra-violet light. It would be more nearly correct to assume α independent of ν, in which case the final equation becomes,

$$F(\nu) = \left(\frac{A'h\nu}{4\beta}\right)\left(1 - \frac{\nu_0}{\nu}\right)^2. \tag{6-18}$$

Equation (6-17) gives a curve which rises to a maximum at $\nu = 2\nu_0$, as shown in Fig. 6-4, while Eq. (6-18) has no maximum. Hence no comparison with experimental curves can be made without more definite information as to the variation of α. It might be remarked, however, that if α be assumed to vary as $1/\nu$, the equation reduces to,

$$F(\nu) = B\left(1 - \frac{\nu_0}{\nu}\right)^2, \; B = \text{const},$$

which is the empirical equation which was found by Werner and Becker[1] to fit closely many experimental curves.

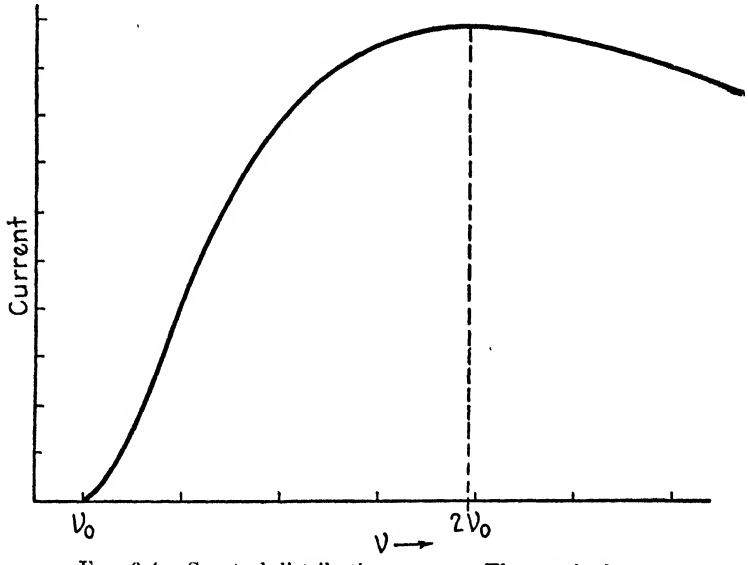

FIG. 6-4.—Spectral distribution curve on Thomson's theory.

Thomson actually developed the above theory not for the purpose of obtaining an expression for the spectral distribution function but to obtain an equation for the voltage-current curve for photoelectrons emitted by a plate and collected by a parallel plate to which was applied a retarding potential V. In order to reach the collecting plate the electrons must arrive at the surface of the illuminated plate with a normal velocity component such that $\frac{1}{2}mv_n^2 > h\nu_0 + Ve$. If in the above analysis we write $h\nu_0 + Ve$ in place of $h\nu_0$, we obtain finally for the rate at which electrons reach the collecting plate,

$$R = B\left[1 - \left(\frac{h\nu_0 + Ve}{h\nu}\right)\right]^2,$$

where B does not depend on V. This is the relation used by Thomson. Plotting R against V gives the parabola shown in Fig. 6-5 as the desired voltage-current curve. The first derivative of this curve is the straight line shown, which is really a distribution curve for the *normal component of the kinetic energy*[2] of the emitted electrons. Thomson found his experimental curves to be of this form and actually used such curves to analyze the radiation produced by an electric discharge through gases.

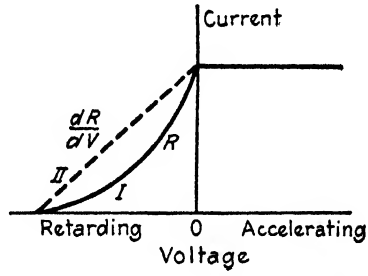

FIG. 6-5.—Theoretical voltage-current (I) and velocity distribution (II) curves. (*Thomson.*)

[1] A. BECKER, *Handbuch der Experimentalphysik*, Vol. XXIII, 1205 (1928).

[2] Kinetic energy, being a scalar quantity, can of course have no components. This is a convenient name, however, for the quantity $\frac{1}{2}mv_n^2$ where v_n is the normal component of the velocity.

6-12. Uspensky's theory differs from that of J. J. Thomson in that a different law of force is assumed to govern the motion of the electrons within the metal. Uspensky assumes that the motion of the electrons is resisted by a viscous force proportional to the velocity, *i.e.*,

$$F_v = -kv.$$

An electron starting with an initial velocity v after traversing a distance l will have the velocity v_l such that,

$$v_l = v - \frac{kl}{m},$$

where m is the electronic mass. In this case the calculations are slightly more complicated and give the final result,

$$F(\nu) = \left(\frac{G_1G_2}{\nu}\right)\left(\sqrt{\frac{\nu}{\nu_0}} + \sqrt{\frac{\nu_0}{\nu}} - 2\right), \tag{6-19}$$

where G_1 is a factor containing only universal constants and G_2 depends on the nature of the metal. In the derivation it has also been assumed that α, the coefficient of absorption for the radiation, is independent of the frequency.

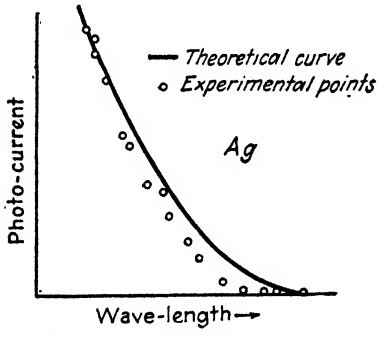

FIG. 6-6.—Comparison of Uspensky's theoretical spectral distribution curve with Suhrmann's observations for Ag.

Uspensky's equation is plotted in Fig. 6-6, together with experimental points obtained by Suhrmann[1] for Ag. The constant G_2 was first determined from the data for one particular frequency, using Suhrmann's value for ν_0. The whole curve can then be plotted and it will be noted that the other experimental points fit it fairly well. The theoretical curve goes through a maximum for $\nu = 9\nu_0$ which in all cases would be far in the ultra-violet.

6-13. Summary.—In conclusion, it must be said that the classical electron theories have not yielded a satisfactory expression for the spectral distribution function. The theories of Richardson and Thomson predict approximately the correct values for the spectral maxima, but the curves are not at all of the same shape as those obtained experimentally. On the other hand, Uspensky's equation seems to reproduce quite well the general shape of the observed curves in the vicinity of the threshold, but predicts a value for the position of the spectral maximum which certainly cannot be reconciled with the data on alkali metals. As we shall see, the newer theories of Sommerfeld, Wentzel, and others

[1] R. SUHRMANN, *Zeits. f. Phys.*, **33**, 63 (1925).

have been somewhat more successful in this direction, but the complexity of the problem and the meagerness and uncertainty of the experimental data may offer for some time to come troublesome obstacles in the way of a complete quantitative solution.

6-14. Relation between the Photoelectric and Thermionic Effects.[1]— Richardson's theory of electron emission outlined in Sec. **6-10** leads to the following equation for the electron current from a metal surface under equilibrium conditions,

$$I = AT^2\epsilon^{-\frac{b_0}{T}} \tag{6-11}$$

As has been pointed out, since the reasoning on which this equation was derived is based purely on thermodynamics, the equation should hold, no matter what the exact mechanism by which the electrons are released from the metal may be, *i.e.*, whether it is a photoelectric or a thermionic process or a combination of the two. As is well known, the equation represents with considerable accuracy the way in which the thermionic current from a pure metal surface depends on the temperature T of the surface. Now it will be recalled that b_0 is simply an abbreviation for L_0/R, where L_0 is the heat of evaporation of one mol of electrons at 0°K and R is the gas constant. We may set $L_0/R = b_0 = \phi_0 e/k$ where k is the Boltzmann constant, and ϕ_0 is the work function of the surface, measured at 0°K. It is evident that ϕ_0 must be the same, whether the electrons are released by a thermionic or a photoelectric process. Now b_0 can be obtained directly from thermionic measurements by the method given in Sec. **3-8**, and the photoelectric work function can be obtained at room temperature by measuring the threshold frequency for the surface and using the relation,

$$h\nu_0 = \phi_0 e.$$

Since experiment shows that the threshold frequency is, to a first approximation, independent of temperature, we arrive at once at the important conclusion that, for all metals for which ν_0 is constant at low temperatures, the *measured* values of the photoelectric and thermionic work functions should be identical, *i.e.*, $h\nu_0 = b_0 k$. The experimental verification of this relation for pure metals has been discussed in Sec. **3-21**.

In case ν_0 depends on the temperature, a more detailed study of the relation between the two work functions is necessary. It has long been recognized that the simple thermodynamic argument by which Eqs. (6-10) and (6-11) are derived is incomplete, since a number of potentially important factors have been neglected; and there has been an extensive discussion, which cannot be reviewed here, as to a more precise method of deriving the thermionic equation. The result has been a more thor-

[1] A thorough review of the subject of thermionic emission, to which the authors are indebted, has been given by S. Dushman, *Rev. Mod. Phys.*, **2**, 381 (1930).

ough understanding of the significance of the various quantities involved and the conclusion has been reached that for clean metal surfaces there should still be an approximate equality between the measured values of the photoelectric and thermionic work functions.

Richardson showed on the basis of the Nernst heat theorem that the constant A in Eq. (6-11) should be a universal constant for all metals, and its value has been calculated by Dushman,[1] making use of the Sackur-Tetrode value of the entropy constant for a perfect gas. He found

$$A = \frac{2\pi k^2 me}{h^3}, \tag{6-20}$$

and if the thermionic current is expressed in amperes per square centimeter of emitting surface, the numerical value of A should be approximately 60. This value has been found experimentally by Dushman and his co-workers,[2] Zwikker,[3] and Goetz[4] for the metals W, Mo, Ta, Cu, and Au. However, there are some surfaces, particularly coated surfaces and Pt, for which the observed values of A are far from the theoretical value. Furthermore, it has been shown by a number of observers[5] that high values of A are always associated with high values of b, and *vice versa*. In fact, for a given surface it appears that a change in b is always accompanied by a change in A such that $\log A$ is a linear function of b.

A number of attempts have been made to give an explanation of these departures of the observed values of the thermionic coefficient from its theoretical value. In the case of coated or composite surfaces it is probable that these departures may be attributed[6] to one of the following causes: (1) changes in the nature of the surface with temperature during the measurements (*e.g.*, oxidized tungsten); (2) errors introduced in the extrapolation of observed values to zero accelerating field, using the Schottky relation which does not hold for such surfaces; (3) reduction of the surface transmission coefficient by the presence of "hills" in the surface potential barrier (see Sec. **6-27**).

For the case of clean metal surfaces, however, it appears that observed values of A differing from 60 may be attributed to the fact that the surface work function is not quite independent of temperature as has been assumed in the derivation of Eq. (6-11). There is thus a close relation between the variations of A and the temperature dependence of the

[1] S. Dushman, *Phys. Rev.*, **21**, 623 (1923).

[2] S. Dushman, Rowe, Ewald, and Kidner, *Phys. Rev.*, **25**, 344 (1925).

[3] C. Zwikker, *Proc. Amst. Acad. Sci.*, **29**, 792 (1926).

[4] A. Goetz, *Zeits. f. Phys.*, **43**, 531 (1927).

[5] For a tabulation of values see S. Dushman, *Rev. Mod. Phys.*, **2**, 381 (1930); L. A. DuBridge, *Proc. Nat. Acad. Sci.*, **14**, 788 (1928); C. Zwikker, *Phys. Zeits.*, **30**, 578 (1929).

[6] S. Dushman, *Rev. Mod. Phys.*, **2**, 381 (1930).

photoelectric threshold, the various aspects of which have been discussed by Schottky,[1] DuBridge,[2] Becker and Brattain,[3] Bridgman,[4] and Herzfeld.[5]

Bridgman shows that a number of aspects of the photoelectric problem can be treated from the viewpoint of pure thermodynamics. For example, imagine two metals connected together and facing each other in an evacuated uniform temperature enclosure (Fig. 6-7). Let the threshold frequencies of the two surfaces be ν_{0A} and $\nu_{0B}(\nu_{0B} > \nu_{0A})$ and let the enclosure be flooded by radiation whose frequency is just equal to ν_{0B}. Then, if equilibrium conditions prevail, no electrons will be released from B and it is evident that for equilibrium there must be no circulation of electrons, hence those released from A must just be stopped on reaching B by the contact-potential difference between A and B: V_{AB}. Hence we have,

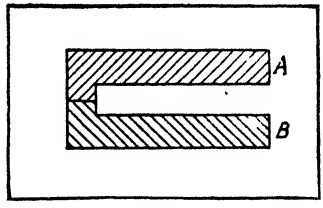

FIG. 6-7.—Photoelectric effect under equilibrium conditions.

$$eV_{AB} = h(\nu_{0B} - \nu_{0A}),$$

the right-hand side representing the energy with which electrons are released from surface A when illuminated by light of frequency ν_{0B}. This is the stopping potential relation discussed in Chapter II and arrived at empirically by Millikan.

It can further be seen that if the enclosure is flooded by radiation of frequency ν greater than either ν_{0A} or ν_{0B} the total number of electrons leaving B must be just equal to the number leaving A. Call this number $f(\nu,T)$. (This function differs from the ordinary spectral distribution function $F(\nu)$ in that it includes the number of electrons reflected from the surface as well as those ejected by the light.) Then $f(\nu, T)$ must be a universal function of ν and T, independent of the metal, that is of ν_0. We may apply this condition together with the condition that the total number of electrons in equilibrium with a surface is independent of whether they are released by a photoelectric or thermionic process. Using an equation which he developed for thermionic emission, including factors which had been neglected by Richardson and others, Bridgman, after some calculation which need not be reproduced, arrives at the following conclusions:

1. When the threshold frequency is independent of the temperature the difference $(h\nu_0 - b_0k)$ should be a universal constant. Since experi-

[1] W. SCHOTTKY, *Handbuch der Experimentalphysik*, Vol. XIII, p. 1 (1928).
[2] L. A. DUBRIDGE, *Proc. Nat. Acad. Sci.*, **14**, 788 (1928).
[3] J. A. BECKER and W. BRATTAIN, *Phys. Rev.*, **37**, 462 (1931).
[4] P. W. BRIDGMAN, *Phys. Rev.*, **27**, 173 (1926); **31**, 90 (1928); **31**, 862 (1928).
[5] K. F. HERZFELD, *Phys. Rev.*, **35**, 248 (1930).

ments show that this difference is probably zero for tungsten, rhodium, and platinum, it must then be zero for all metals. Exact analysis thus confirms the conclusion regarding the equality of thermionic and photoelectric work functions.

2. In case ν_0 varies with temperature, the above relation still holds, provided we understand by ν_0 the value of the threshold measured at 0°K. In most cases this is probably not greatly different from the value observed at room temperatures.

3. If ν_0 is a function of T, then the thermionic equation is modified and must be written in the form,

$$I = A\epsilon^{-\alpha} T^2 \epsilon^{-\frac{b_0}{T}} = A'T^2\epsilon^{-\frac{b_0}{T}}, \quad A' = A\epsilon^{-\alpha} \tag{6-21}$$

where $\alpha = (h/k)\,(d\nu_0/dT)$, and A is the usual universal constant. Hence the observed value of the coefficient A' will differ from A by the factor $\epsilon^{-\alpha}$. A relative temperature coefficient of only 3×10^{-4} per degree would cause the observed value A', to differ from the theoretical by a factor of 1.3×10^7. It seems possible to account for the observed values of A' on this basis.

We have already mentioned[1] Herzfeld's theory in which he shows that the temperature coefficient of the photoelectric threshold should be proportional to the volume coefficient of expansion of the metal. From Eq. (6-3),

$$\frac{d(h\nu_0)}{dT} = -q_2\beta.$$

Herzfeld deduces also Eq. (6-21) used by Bridgman, and it follows that α should have the value,

$$\alpha = -q_2\frac{\beta h}{k}.$$

Herzfeld points out that the differences in β among the various metals are sufficient to account for large variations in A, although it can be shown that for the particular case of tungsten and platinum the difference in the values of β is not great enough to account for the observed difference in the values of A.

Bridgman's conclusion (2), mentioned above, points to the fact that the equality between the photoelectric and thermionic work functions is only approximate when one or both depend on the temperature. This question has recently been discussed from a different viewpoint by Becker and Brattain, who make use of the fact that the thermionic work function, as determined from the slope of a Richardson plot, is a measure of the change in *total* energy of an electron in passing through a metal surface, while Bridgman and Herzfeld have shown that the photoelectric

[1] See Sec. 6-6.

work function is probably determined by the change in *free* energy. Consequently, if they are measured at the same temperature, the relation between the measured quantities b_0 and ν_0 is shown to be given by,

$$b_0 k = h\left(\nu_0 - T\frac{d\nu_0}{dT}\right).$$

More accurate values of b_0, ν_0 and their temperature coefficients are needed before this relation can be checked. It predicts a difference between the measured values of the thermionic and photoelectric work functions of the order of 2 per cent in some cases.[1]

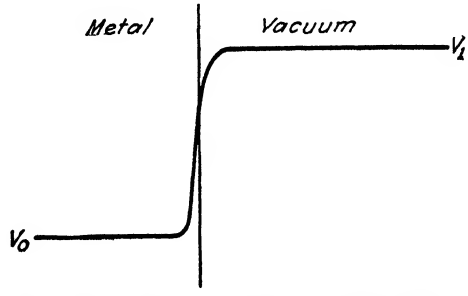

FIG. 6-8.—Potential barrier at metal surface.

6-15. The Nature of the Surface Work Function.—We may now consider briefly, on the basis of classical theory, the nature of the forces at metal surfaces which give rise to the work function. Both photoelectric and thermionic experiments show clearly that an amount of energy, ϕe, is required to extract an electron from a metal surface. The quantity ϕ, the work function, is thus simply the effective potential difference through which an electron must pass in leaving the surface. Since the region within the body of the metal can be regarded as one of constant potential, it is evident that this jump in potential must take place in a very thin surface layer. The potential variation through the surface may then be pictured as taking place in the manner shown in Fig. 6-8. Now ϕe is the *net* energy required to remove an electron from the metal. Hence ϕ will be equal to the actual potential difference across the surface $(V_1 - V_0)$ minus E_k/e, the amount of energy already possessed by the electron inside the metal. On the classical theory of metals

$$E_k = \tfrac{3}{2}kT,$$

which at ordinary temperatures corresponds to an electron energy of

[1] R. H. FOWLER (*Phys. Rev.*, **38**, 45 [1931]) has shown that the thermal energies of the electrons may cause an *apparent* change of ν_0 with T, so that $(d\nu_0/dT)$ *as ordinarily measured* loses all quantitative significance. The above arguments hold only if there is a change of the *true* threshold with temperature and no such change has as yet been detected (see Sec. **6-30**).

only 0.01 volt. Hence it may be neglected in comparison with the total work function, which is of the order of 4 volts. Therefore on the classical theory, we have approximately,

$$V_1 - V_0 = \phi.$$

This relation is worthy of mention because it no longer holds in the Sommerfeld theory.

For many purposes it is sufficient merely to know that such a surface work function does exist; but a satisfactory *explanation* of its existence and a method for *calculating* its value for different metals would be of great value, and would serve to shed much light on the important and perplexing problem of the nature of metal surfaces and surface forces. This problem has not been solved, and we can only indicate the progress which has been made.

In the first place, it can be seen that a potential jump such as that shown in Fig. 6-8 would be present if there existed at the surface an electric double layer with the negative charges on the outside. The concept of such a double layer is an extremely useful one and has often been used, particularly by Richardson and Wilson,[1] in describing work-function phenomena. Unfortunately, there is no independent evidence of the existence of such double layers on clean metals, and the concept has not been employed to obtain quantitative results.

Debye[2] and Schottky[3] have made the assumption that the work function can be accounted for on the basis of the "image force" on the electron when near the conducting surface. For an electron at a distance x from the surface the magnitude of the image force is $e^2/4x^2$, and the potential at this point is $e/4x$ when the potential at infinity is taken as zero. This alone would give an infinite potential for points on the surface, and hence an infinite amount of energy would be required to remove an electron. It is therefore assumed that the image law breaks down for points close to the surface, *i.e.*, for x smaller than some critical value x_0. Within this region the force on the electron is taken as constant,[4] equal to $e^2/4x_0^2$. The total work done in removing an electron from the surface is then,

$$\phi e = \int_0^{x_0}\left(\frac{e^2}{4x_0^2}\right)dx + \int_{x_0}^{\infty}\left(\frac{e^2}{4x^2}\right)dx.$$

[1] H. A. Wilson, *Phil. Trans. Roy. Soc.*, (A) **208**, 268 (1908).

[2] P. Debye, *Ann. d. Phys.*, **33**, 441 (1910).

[3] W. Schottky, *Zeits. f. Phys.*, **14**, 63 (1923).

[4] This assumption is rather arbitrary and actually unnecessary. The results obtained are independent of the variation of the field very close to the surface as long as it is such as to yield a finite work function. See I. Langmuir and K. T. Compton, *Rev. Mod. Phys.*, **2**, 124 (1930).

Hence,

$$\phi = \frac{e}{2x_0}. \tag{6-22}$$

For the case of tungsten, for which $\phi = 4.5$ volts, we have,

$$x_0 = \frac{300 \cdot 4.77 \cdot 10^{-10}}{2 \cdot 4.5}$$

$$= 1.59 \cdot 10^{-8} \text{ cm.}$$

Thus x_0 is of the order of the distance between atoms which for tungsten is 2.7×10^{-8} cm. If we identify x_0 with the atomic separation, then Eq. (6-22), above, leads to the expectation that the values of the work function for different metals will be inversely proportional to x_0. This is consistent with the fact that when in Chapter III we plotted work functions as a function of atomic number, we obtained a curve similar in appearance to an inverse atomic-volume curve, with pronounced minima for the alkali metals. A more exact test of the equation cannot be made because of the uncertainty in the values of ϕ.

There is additional qualitative evidence for this theory in the observations on the change in work function through melting and transition points. Goetz[1] found that the work function was greater for the phase of greater density, *i.e.*, of smaller atomic separation. This is in the proper direction to be accounted for by the theory.

(The above theory meets with a serious difficulty, however, in connection with the Sommerfeld electron theory, on the basis of which it appears that the actual fall in potential at metal surfaces (W_a) is two to four times greater than the work function ϕ, on account of the large electron energies in the metal. Then if W_a equals, say, 15 volts Eq. (6-22) gives $x_0 = 4.76 \times 10^{-9}$ cm, which is five times smaller than the atomic separation. At such distances from the surface the image law has no meaning. Hence it must be concluded that the pure image field can account for only a small part [of the order of $\frac{1}{3}$] of the total surface work function.)

The Schottky theory has, however, been applied successfully to the problem of electron emission in accelerating fields. It is well known that photoelectric and thermionic currents from a metal never become completely saturated even for large accelerating potentials, but continue to increase with increasing fields. This effect, commonly known as the Schottky effect, is explained as follows:[2]

Let the force on an electron at a distance x from a metal surface be $F(x)$. The work function of the surface is then given by

$$\phi e = \int_0^\infty F(x)dx.$$

[1] A. Goetz, *Phys. Rev.*, **33**, 373 (1929).

[2] *Cf.* I. Langmuir and K. T. Compton, *Rev. Mod. Phys.*, **2**, 124 (1930).

If now an electric field F_a/e is applied at the surface, the resultant force on the electron will be $(F[x] - F_a)$ and the potential V at a point x is given by

$$eV = \int_0^x (F[x] - F_a)dx,$$

which will be of the form shown in Fig. 6-9. The effective work function will now be lower for two reasons: first, because the force is less;

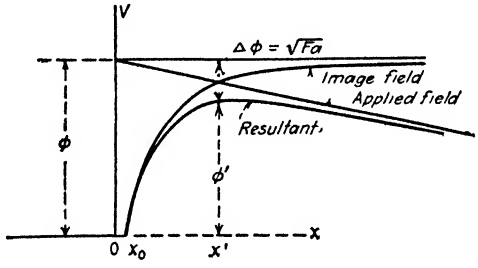

FIG. 6-9.—Reduction of surface work function by an applied field (Schottky effect).

and second, because it is no longer necessary to remove the electron to infinity, but only to the point x' where the force due to the applied field just neutralizes the attracting force toward the surface. The work function will then be

$$\begin{aligned} e\phi' &= \int_0^{x'} (F[x] - F_a)dx, \\ &= \int_0^\infty F(x)dx - \int_{x'}^\infty F(x)dx - \int_0^{x'} F_a dx, \\ &= e\phi - \int_{x'}^\infty F(x)dx - F_a x'. \end{aligned} \tag{6-23}$$

If we assume that at distances from the surface greater than x', $F(x)$ is merely the image force $e^2/4x^2$, then at the point x',

$$e^2/4x'^2 = F_a,$$

or

$$x' = \left(\frac{e}{2\sqrt{F_a}}\right). \tag{6-24}$$

Equation (6-23) then becomes,

$$e\phi' = e\phi - \left(\frac{e^2}{4x'}\right) - F_a \cdot \left(\frac{e}{2\sqrt{F_a}}\right)$$

or,

$$\phi' = \phi - \sqrt{F_a}. \tag{6-25}$$

This equation has been subjected to considerable experimental test for the case of thermionic emission. If the above value of ϕ' is substituted in the Richardson equation,

$$I = AT^2\epsilon^{-\frac{\phi' e}{kT}},$$

we may at once deduce the relation,

$$I = I_0\epsilon^{\frac{e\sqrt{F_a}}{kT}} \tag{6-26}$$

where I_0 is the current for zero external field. Since for a given arrangement of electrodes the field F_a is directly proportional to the potential difference V applied between anode and cathode, it follows at once from Eq. (6-26) that if I is measured as a function of V, then, on plotting log I against $\sqrt{V}$, a straight line should be obtained. Such curves obtained by Pforte are shown in Fig. 6-10. The relation has been verified[1] for clean metal surfaces for fields up to 10^6 volts/cm. (At higher fields the "cold discharge" begins and this theory no longer applies.) These experiments prove that for clean metals the force on an electron at distances from the surface greater than x' is approximately the image force. The order of magnitude of the distance x', at which the surface forces are just neutralized by the applied field, is easily computed from Eq. (6-24). Thus, for a field of 10^6 volts/cm, $x' = 19 \times 10^{-8}$ cm and for a field of 100 volts/cm, $x' = 19 \times 10^{-6}$ cm. Hence x' is always considerably greater than atomic dimensions and it would be expected that the image law should hold.

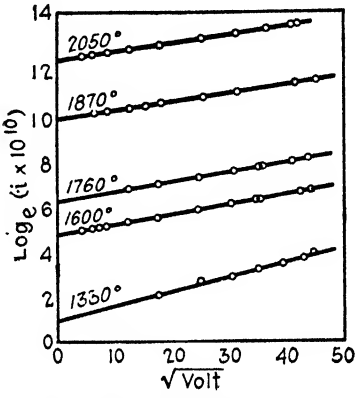

FIG. 6-10.—Experimental verification of Schottky's equation. (*Pforte.*)

For the case of composite surfaces, such as thoriated tungsten, however, experiments show that there are wide deviations from the Schottky relation, particularly at low fields. This shows that for such surfaces there are other forces in addition to the image force. The above theory can be used, however, to study the nature of these forces. Differentiating the Richardson equation with respect to F_a, we get, if A does not depend on F_a,

$$\frac{d(\log I)}{dF_a} = -\left(\frac{d\phi'}{dF_a}\right)\cdot\frac{e}{kT}$$

But from Eq. (6-23), which does not involve the image law, we see at once, since ϕ does not depend on F_a,

$$e\frac{d\phi'}{dF_a} = F(x')\frac{dx'}{dF_a} - x' - F_a\frac{dx'}{dF_a} = -x', \tag{6-26a}$$

[1] W. S. PFORTE, *Zeits. f. Phys.*, **49**, 46 (1928); N. A. DE BRUYNE, *Proc. Roy. Soc.*, **120**, 423 (1928).

since by assumption $F(x') = F_a$. Hence we have finally

$$\frac{d(\log I)}{dF_a} = \frac{x'}{kT}.$$

Therefore the slope of the $\log I$ vs F_a curve at any value of F_a determines the distance x' at which the applied field F_a is just equal to the surface field.

This method of exploring surface fields has been employed by Becker and Mueller,[1] who have found that for thoriated tungsten there are fields

> . . . which close to the surface are very large and in such a direction as to help the electrons escape; at larger distances they are in the opposite direction and may be of an appreciable magnitude as far out as 2500 thorium-atom diameters. The huge fields close to the surface are responsible for the decreased work function (caused by the adsorbed thorium), while the reverse fields farther out are the cause of the lack of saturation (always observed with such surfaces).[2]

The nature and cause of the surface fields which give rise to these departures from the Schottky relation are not fully understood. Langmuir[3] and others have accounted qualitatively for certain features of the phenomenon by the assumption that the surface is covered with patches whose work function is lower than that of the pure metal. Becker and Mueller[4] have been able to account for some of their results by assuming that the layer of electropositive ions on the surface acted as the grid of a thermionic tube. In a critical review of these theories Langmuir and Compton[5] have recently pointed out that neither is able to account quantitatively for all the observed facts.

The application of the Schottky effect to photoelectric emission offers an interesting and important field of investigation which has as yet scarcely been touched, except for the work of Lawrence and Linford,[6] discussed in Sec. **3-31**. Equation (6-25) should apply to the photoelectric as well as the thermionic work function, and hence the photoelectric threshold should show a decrease proportional to the square root of the applied field, and therefore photoelectric currents should never become completely saturated. This is in agreement with the results of Lawrence and Linford. Furthermore, we have at once from Eq. (6-26*a*)

$$\frac{d\nu_0}{dF_a} = \frac{e}{h}\frac{d\phi'}{dF_a} = -\frac{x'}{h}.$$

The slope of the ν_0 vs. F_a curves thus is a measure of x', the distance from the surface at which the surface force is equal to the applied force F_a,

[1] J. A. Becker and D. Mueller, *Phys. Rev.*, **31**, 431 (1928).
[2] Quoted from J. A. Becker and D. Mueller, *loc. cit.*
[3] I. Langmuir, *Gen. Elec. Rev.*, **23**, 504 (1920).
[4] J. A. Becker and D. Mueller, *loc. cit.*
[5] *Loc. cit.*
[6] E. O. Lawrence and L. B. Linford, *Phys. Rev.*, **36**, 482 (1930).

and hence the magnitude of the surface fields at various distances from the surface can be determined from photoelectric as well as thermionic measurements. In Fig. 6-11, taken from the paper by Lawrence and Linford, the curves A, B, and C represent the threshold shifts with applied field for thin films of potassium on tungsten prepared in different ways. The curves D represent the fields at various distances from the surface, as deduced from these curves. The full lines in each case represent the curves to be expected in case the fields are due only to the image force, and the actual curves were of this form for certain types of surfaces.

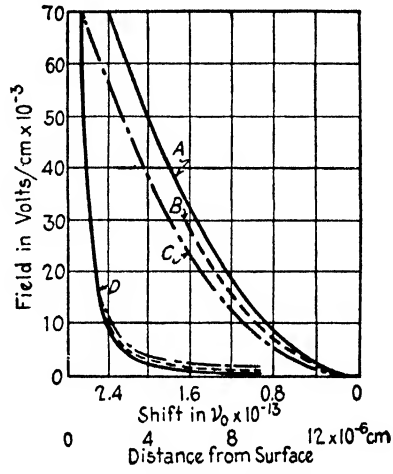

FIG. 6-11.—Schottky effect in photoelectric emission. Curves A, B, and C represent the shift in ν_0 with applied field for various potassium surfaces; curves D represent the surface fields deduced therefrom. The full curves in each case are for a pure image field.

Quite recently Bartlett and Waterman[1] have pointed out that the Schottky theory rests on the assumption that the fields due to space charge of the electron atmosphere just outside the metal surface are negligible in comparison with the image field. While this assumption is quite justified when a Maxwellian distribution of electrons is postulated, it no longer holds for a Fermi distribution. The above authors have worked out a theory in which the image field is assumed to be negligible in comparison with the space-charge effects, and they have succeeded in predicting the proper variation of thermionic current with applied field for both clean and composite surfaces. Furthermore, the space-charge field gives rise quite naturally to a surface potential barrier of 10 to 15 volts, as required by the Sommerfeld theory.

6-16. Is Thermionic Emission Really a Photoelectric Effect?—We have seen that the thermodynamical theory of Richardson presented in Sec. **6-10** leads to the conclusion that the photoelectric current from a metal which is illuminated by the radiation from a black body at the temperature T varies with T in the same way as the thermionic current from a hot body. This conclusion has been amply confirmed by the experiments of W. Wilson,[2] A. Becker,[3] and Roy.[4] Bridgman[5] has shown

[1] R. S. BARTLETT and A. T. WATERMAN, *Phys. Rev.*, **37**, 279 (1931); R. S. BARTLETT, *Phys. Rev.*, **37**, 959 (1931); A. T. WATERMAN. *Phys. Rev.*, **38**, 1497 (1931).

[2] W. WILSON, *Proc. Roy. Soc.*, **93**, 359 (1917).

[3] A. BECKER, *Ann. d. Phys.*, **78**, 83 (1925).

[4] S. C. ROY, *Proc. Roy. Soc.*, **112**, 599 (1926).

[5] P. W. BRIDGMAN, *Phys. Rev.*, **31**, 90 (1928).

that the velocity distribution of the photoelectrons will also be the same as for the thermionic electrons, and this has been confirmed by A. Becker. In fact, Bridgman has reached the general conclusion that for a metal in equilibrium with its temperature radiation and with its electron vapor, *all* the conditions of equilibrium will be the same whether the electrons are ejected from the metal by a thermionic or a photoelectric process, or by the two working conjointly in any ratio. Thermodynamics is in fact "unable to distinguish between or even give separate meaning to the two mechanisms under equilibrium conditions."

These conclusions very naturally lead one to make the obvious and appealing assumption that the thermionic effect itself is really a photoelectric phenomenon, due to the action of the temperature radiation within the hot metal on itself. This suggestion of an "autophotoelectric effect" was first made and discussed by Richardson[1] in 1912, and has been considered by many subsequent writers. Richardson recognized, and Bridgman has further emphasized, the fact that, although the above thermodynamic arguments make this suggestion plausible, they can give no direct evidence as to its actual truth, since thermodynamics has nothing to say about the *mechanism* by which equilibrium conditions are attained. The truth of the autophotoelectric hypothesis therefore must be tested by considerations of a different sort, and it has been recognized that it depends primarily on the question of whether the numerical values of the photoelectric efficiency are sufficiently large to enable the temperature radiation within a body to eject enough electrons to account for the relatively large thermionic currents which may be drawn from it. Richardson has concluded from a consideration of experimental values that *even in the most favorable cases* the photoelectric emission from a surface due to its own temperature radiation would be 5000 times smaller than the measured thermionic currents.

It must be recalled, of course, that in the photoelectric effect, light from an outside source is focused on a cold metal and is quickly absorbed in a thin surface layer; hence only the electrons very near the surface have a chance of being ejected. In a hot body, on the other hand, radiation permeates the entire body and may release photoelectrons at any depth. However, experiments on the photoelectric effect in thin films indicate that the mean free path for electrons in a metal is quite small (approximately 100 atomic diameters, according to the Sommerfeld theory), and hence only electrons near the surface can escape in any case. Furthermore, Ives[2] has found that measurable thermionic currents may be obtained from a thin film of caesium on platinum when the temperature of the platinum is below 800°C and hence is just beginning to emit visible radiation; but to obtain photoelectric currents of the same order of magnitude, it is necessary to focus on the surface the brilliant image of an automobile headlight lamp. He took this to be evidence against the autophotoelectric hypothesis, since in these experiments the films of alkali metal were so thin that

[1] O. W. Richardson, *Phil. Mag.*, **23**, 618 (1912); **31**, 149 (1916); "Emission of Electricity from Hot Bodies," 2d ed. p. 110 (Longmans, Green & Co., 1921).

[2] H. E. Ives, *Astrophys. Jour.*, **64**, 128 (1926).

every Cs atom was essentially a surface atom and the incident radiation easily penetrated the entire film. It is possible, however, that the photoelectric and thermionic currents from such films originate largely in the underlying metal, the film acting merely to reduce the work function. The experiments are thus not conclusive. Nevertheless, the present evidence indicates that at best the autophotoelectric effect contributes but an insignificant portion of the total thermionic emission. Furthermore, the Sommerfeld electron theory gives an adequate account of thermionic emission without making use of the photoelectric process.

II. THE SOMMERFELD ELECTRON THEORY[1]

6-17. Introduction.—In 1927 an entirely new conception of the condition of electrons in metals was introduced by Pauli,[2] who discarded the notion that the free electrons could be treated as a perfect gas obeying classical statistics, and assumed that they must be treated as a degenerate gas obeying the new statistics of Fermi[3] and Dirac.[4] On this assumption he gave a satisfactory explanation of the paramagnetic susceptibility of alkali metals at low temperatures. Sommerfeld[5] at once applied this assumption to problems of electronic conduction in metals, and in a series of important papers laid the basis for a new theory of metals which has had conspicuous success in many directions. For example, Sommerfeld's theory leads to satisfactory expressions for the thermal and electrical conductivity and gives a value of the Wiedemann-Franz ratio in excellent agreement with experiment. It avoids the old specific-heat difficulty, since the electron energies are independent of temperature. Furthermore, it yields for the first time values of the thermoelectric coefficients which are of the right order of magnitude and show the correct dependence on temperature. The theory has been extended to problems in photoelectric and thermionic emission by Sommerfeld,[6] and by Fowler and Nordheim,[7] Wentzel,[8] and others.[9]

An excellent and concise review of the basis of the new theory has been published by Darrow;[10] and Nordheim[11] has summarized its applica-

[1] The treatment of this subject is based principally on a series of lectures given by Prof. L. Brillouin at the University of Michigan during the summer of 1929. See L. Brillouin, "Les Statistiques Quantique" (Les Presses Universitaires de France, 1930).

[2] W. Pauli, *Zeits. f. Phys.*, **41**, 81 (1927).

[3] E. Fermi, *Zeits. f. Phys.*, **36**, 902 (1926).

[4] P. A. M. Dirac, *Proc. Roy. Soc.*, **112**, 661 (1926).

[5] A. Sommerfeld, *Zeits. f. Phys.*, **47**, 1 (1928).

[6] *Loc. cit.*

[7] R. H. Fowler, *Proc. Roy. Soc.*, **122**, 36 (1929); R. H. Fowler and L. Nordheim, *Proc. Roy. Soc.*, **119**, 173 (1928); L. Nordheim, *Zeits. f. Phys.*, **46**, 833 (1928); R. H. Fowler, *Phys. Rev.*, **38**, 45 (1931).

[8] G. Wentzel, "Probleme der Modernen Physik," p. 79.

[9] H. Fröhlich, *Ann. d. Phys.*, **7**, 103 (1930); I. Tamm and S. Schubin, *Zeits. f. Phys.*, **68**, 97 (1931).

[10] K. K. Darrow, *Phys. Rev.*, *Supplement*, **1**, 90 (1929).

[11] L. Nordheim, *Phys. Zeits.*, **30**, 177 (1929); also R. H. Fowler, *Nature*, **126**, 611 (1930)

tions to problems of electron emission. No attempt at more than a brief presentation of the theory will therefore be made here, and we shall confine ourselves simply to recalling some of the new concepts which it has introduced, and to a brief discussion of the new theory of the photoelectric effect which it has made possible.

6-18. The Fermi-Dirac Electron Gas.—In the development of the Fermi-Dirac statistics it is assumed that the Pauli exclusion principle[1] can be generalized so that it applies not only to the electrons in a single atom or molecule but to any assembly of electrons. To apply the principle to an electron gas it is assumed that each electron is represented by a point in a six-dimensional phase space whose coordinates are the position and momentum components of the electron. The "phase space" is then divided up into "elementary cells," each of volume h^3, and the generalized Pauli principle asserts: Each elementary cell can be occupied by the representative point of *not more* than *one*, or, if their spin axes are reversed, *two* electrons. This assumption leads to a distribution function of the form,

$$f = \frac{2}{e^{\alpha + \frac{\epsilon}{kT}} + 1} \tag{6-27}$$

where f is the average number of electrons in each *cell* whose energy is ϵ, and α is a parameter depending only on T and the number of electrons per unit volume (see Eq. [6-28] below). It is evident that the form of the function will depend primarily on the numerical value of α. Thus, if α is a large positive number, the exponential factor in the denominator will be large compared to unity, and the function reduces to a simple exponential (Maxwellian) distribution. On the other hand, if α is a large negative number (*i.e.*, larger than about 10), then, for small values of ϵ (which is always positive), the whole exponential term in the denominator is small compared to unity and we have simply, $f = 2$. As ϵ increases, f retains approximately this constant value but, in the neighborhood of the point where $-\epsilon/kT = \alpha$, f drops exponentially to 0, as shown in Fig. 6-12. The exponential drop is actually discontinuous for $T = 0°K$, and is quite sharp even for high temperatures.

Now Sommerfeld has shown that, for the free electron gas in a metal, α is in all cases a large negative number, and hence the energy distribution function is of the type shown in Fig. 6-12 and not of the type given by classical statistics. For the case in which α is negative its value may be computed from the equation,[2]

[1] W. Pauli, *Zeits. f. Phys.*, **31**, 765 (1925).

[2] This equation for α is obtained by integrating Eq. (6-27) over all cells in the phase space and setting the result equal to n the total number of electrons in unit volume. See A. Sommerfeld, *loc. cit.*

$$\alpha = -\left(\frac{h^2}{2mkT}\right)\left(\frac{3n}{8\pi}\right)^{\frac{1}{3}}, \tag{6-28}$$

where n is the number of electrons per unit volume. Thus for silver at 300°K, assuming one free electron per atom, we have,

$$\alpha = -231.$$

Even at the highest attainable temperatures, α is a sufficiently large negative number that the electron gas must be considered as completely "degenerate"—obeying the Fermi rather than the classical statistics.

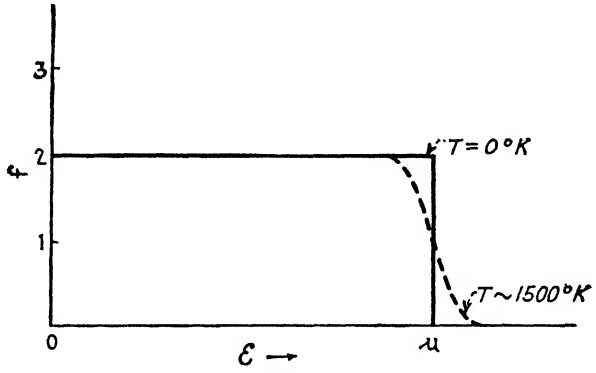

FIG. 6-12.—The Fermi-Dirac distribution function. ($u = -\alpha kT$.)

6-19. The velocity distribution function for the electrons can be obtained directly from Eq. (6-27). Let dn be the number of electrons in unit volume whose velocity components ξ, η, ζ lie in the range $d\xi$, $d\eta$, $d\zeta$. Their representative points in the phase space will occupy the hyper-volume $m^3 d\xi d\eta d\zeta$. Dividing this by h^3 to get the number of elementary cells in this volume and multiplying by f, the number of electrons in each cell, we have

$$dn = 2\frac{m^3}{h^3}\frac{d\xi d\eta d\zeta}{e^{\alpha+\frac{\epsilon}{kT}}+1} = f_v d\xi d\eta d\zeta, \tag{6-29}$$

where $\epsilon = (m/2)(\xi^2 + \eta^2 + \zeta^2) = mv^2/2$. This function, f_v, except for a constant factor, is the same as that plotted in Fig. 6-12. It is evident that all velocities are equally probable up to a certain maximum velocity for which $mv^2/2 = -\alpha kT$.

Similarly, we write down for reference the momentum and energy distribution functions which are easily derived from the above. If dn_p is the number of electrons in unit volume whose total momenta lie in the range p, $p + dp$, then, $\epsilon = p^2/2m$ and

$$dn_p = \frac{8\pi p^2}{h^3} \frac{dp}{e^{\alpha + \frac{p^2}{2mkT}} + 1} = f_p dp. \tag{6-30}$$

Also if dn_ϵ is the number of electrons per unit volume whose total kinetic energies lie in the range ϵ, $\epsilon + d\epsilon$,

$$dn_\epsilon = \frac{8\pi}{h^3} \frac{\sqrt{2m^3\epsilon}\, d\epsilon}{e^{\frac{-(\mu-\epsilon)}{kT}} + 1} = f_\epsilon d\epsilon, \tag{6-31}$$

where we have written $\mu = -\alpha kT$. The value of μ can be easily calculated from Eq. (6-28),

$$\mu = \left(\frac{h^2}{2m}\right)\left(\frac{3n}{8\pi}\right)^{\frac{2}{3}}. \tag{6-32}$$

The energy distribution function given by Eq. (6-31) has been plotted in Fig. 6-13, and this curve exhibits the most striking property of the

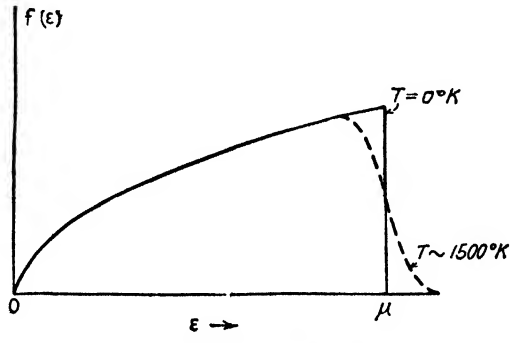

FIG. 6-13.—Fermi-Dirac energy distribution function.

Fermi electron gas. It will be noted that even for $T = 0$ the electrons do not all have zero energy (only two can occupy the cell for which $\epsilon = 0$) but have energies ranging from zero up to a maximum value given by $\epsilon_{max} = \mu$. Now the numerical value of μ for silver, for example, is approximately six electron volts and is independent of the temperature. We are thus confronted with the surprising picture of the electrons, even at the absolute zero, dashing about with energies hundreds of times greater than allowed by the classical theory, even for the highest temperatures.

Returning to the phase space we see that for $T = 0$ all the electrons are crowded into the cells of small momentum. Hence we can describe a "sphere" about the origin of radius p_0 within which all the cells are filled, each with two paired electrons, while the cells outside are empty. The number of cells in a spherical shell of thickness dp is $(4\pi p^2/h^3)dp$ and the total number of cells inside the sphere p_0 must equal half the total number of electrons. That is, for unit volume,

$$\left(\frac{4\pi}{h^3}\right)\int_0^{p_0} p^2 dp = \frac{n}{2}.$$

Integrating we find,

$$p_0 = h\left(\frac{3n}{8\pi}\right)^{\frac{1}{3}},$$

which is the maximum value of the momentum that an electron can have at $T = 0$. It could also have been calculated from Eq. (6-32), using the relation $p_0^2/2m = \mu$.

We can now calculate the total energy of all electrons at absolute zero. It is simply,

$$E_0 = \left(\frac{8\pi}{h^3}\right)\int_0^{p_0} p^2 dp\left(\frac{p^2}{2m}\right),$$

where we have multiplied the expression for the number of electrons in the shell dp by the energy of each electron, $p^2/2m$, and integrated over all cells. This gives at once,

$$E_0 = \left(\frac{3nh^2}{10m}\right)\left(\frac{3n}{8\pi}\right)^{\frac{2}{3}}. \tag{6-33}$$

Hence the average energy per electron is from Eqs. (6-33) and (6-32),

$$\bar{\epsilon}_0 = \frac{E_0}{n} = \tfrac{3}{5}\mu. \tag{6-34}$$

These expressions for the energy and momentum at absolute zero are of importance because Sommerfeld has shown that they are also approximately valid even at high temperatures. The effect of increasing the temperature is simply that some of the electrons which occupied cells within the sphere p_0 move out and occupy cells of larger energy outside the sphere, so that the energy distribution function takes the form indicated by the dotted line in Fig. 6-13. The *relative* number of electrons which attain higher energies is, however, very small, so that the above expressions for the total and average energy of the electrons remain approximately valid. The *actual* number which attain higher energies, however, are sufficient to account for the thermal conductivity, thermionic emission, and other thermal effects in the metal.

6-20. Specific Heat of the Electrons.—Referring to Eq. (6-33) for the total energy of the electrons, we see that this is independent of the temperature and hence, at low temperatures, the specific heat of the electrons is zero. Carrying the calculations to the second approximation, Sommerfeld has shown that the total electron energy may be written in the more exact form,

$$E = E_0 + \tfrac{1}{2}\gamma T^2 \tag{6-35}$$

where γ is a constant. However, the numerical value of γ is such that at 300°K the specific heat of the electrons is less than $\frac{1}{60}$ that of the atoms,

so that the troublesome specific-heat difficulty faced by the classical theory is completely avoided.

6-21. Thermionic Emission.—We shall pass over the applications of the Sommerfeld theory to other fields and come directly to a consideration of its bearing on problems of electron emission. The problem of thermionic emission has been treated in detail by Sommerfeld and by Fowler and Nordheim, who have shown that the new theory leads directly to the Richardson T^2 equation. This is not surprising since this equation can be derived from pure thermodynamical arguments and hence should be derivable from any consistent theory of the mechanism. However, the Sommerfeld theory gives a new interpretation to the constants appearing in the equation, and this is of importance.

In the first place, it is obvious that our ideas of the surface work function need to be considerably revised. For when we were dealing with electrons which were nearly at rest in the metal it was sufficient to suppose that they were held within the metal by a surface potential jump approximately equal to the measured value of the work function, expressed in volts. However, if the electrons have kinetic energies of the order of 6 to 12 volts, it is necessary to assume that the surface potential jump is of the order of 10 to 20 volts—three or four times as large as assumed in the old theory. Let ψ represent the magnitude of the jump in potential at the surface. Then the change in the *potential* energy, when a single electron is removed from the metal, is

$$W_a = \psi e.$$

The change in the *kinetic* energy of the system when an electron is extracted will be given by

$$W_k = -\frac{dE}{dn},$$

where E is the total kinetic energy of all electrons. We shall make no appreciable error if we use for E its value at absolute zero given by Eq. (6-33). Then from Eqs. (6-33) and (6-34)

$$\begin{aligned} W_k &= -\frac{5}{3}\frac{E_0}{n} = -\tfrac{5}{3}\bar{\epsilon}_0 \\ &= -\mu. \end{aligned} \tag{6-36}$$

Therefore the *net* work done in removing an electron is simply $(W_a - \mu)$ and this must equal ϕe where ϕ is the measured value of the work function. The net work function is thus made up of the difference of two terms, W_a depending on the surface potential jump; and μ, depending on the internal kinetic energy of the electrons. It can be shown that

μ is simply the "thermodynamic potential per electron" of the Fermi electron gas.[1]

The method of calculating the number of electrons leaving the surface in thermionic emission can readily be seen. Let dn_ξ be the number of electrons in unit volume having the velocity component ξ normal to the surface in the range $d\xi$. This is obtained by integrating Eq. (6-29) with respect to η and ζ from $-\infty$ to $+\infty$. The number of electrons coming up to unit area of the surface per second then is simply ξdn_ξ. Only those can leave the surface for which ξ is greater than the critical value ξ_0 given by $\frac{1}{2}m\xi_0^2 = W_a$. Integration over all values of ξ from ξ_0 to infinity gives as a final result for the thermionic current per unit area,

$$I = 2AT^2e^{\frac{-(W_a-\mu)}{kT}} \tag{6-37}$$

where A is the universal constant of Dushman having the numerical value 60 amp/cm^2 deg^2. The factor 2 is a result of the factor 2 in Eq. (6-27), due to the electron spin and, as expected, the difference $W_a - \mu$ plays the rôle of the work function.

Most experiments are not sufficiently accurate to determine whether the value 120 for the coefficient fits the data better than the value 60, though the best experiments tend to the smaller value. Fowler and Nordheim,[2] in a more detailed study of this equation, find that it should include also a factor $\overline{D}$, the average transmission coefficient for the electrons through the surface potential barrier. They find that not all electrons with energy greater than W_a will penetrate the barrier, but, on the basis of wave mechanics, a certain number will be reflected back, so that the transmission coefficient may have any value between 0 and 1, depending on the form of the potential variation through the surface. The factor $\overline{D}$ (which might also be called the "electron emissivity" of the surface, since it is analogous to the radiant emissivity) can also be written as $(1 - R)$, where R is the average reflectivity of the surface for electrons. Now Richardson recognized in his earliest derivation of the thermionic equation that this factor $(1 - R)$ should be included, but in the absence of any experimental values assumed R to be zero. Later experiments have shown this assumption to be untenable, yet it has been retained because of the close check between theoretical and experimental values of the thermionic coefficient. The present theory removes the difficulty, since the coefficient now takes the form, $2A(1 - R)$, and Fowler and Nordheim have shown that R in many cases should be of the order of $\frac{1}{2}$, so that the coefficient reduces to $A = 60$. For coated

[1] That is, $\mu = \frac{1}{N}(U - TS)$; see L. Brillouin, "Les Statistiques Quantique," p. 220.

[2] *Loc. cit.*

surfaces R should approach 1 and hence the observed value of the coefficient should be less than 60, which is in agreement with experiment.

6-22. Photoelectric Effect.—We may now consider the picture of the photoelectric process offered by the new theory. This problem has also been discussed by Fowler and Nordheim, and more completely by Wentzel.

As in the older theories, we imagine that a quantum of energy $h\nu$ is conferred upon a free electron whose initial kinetic energy is E_k. Then if $h\nu + E_k \geqq W_a$, the electron may escape from the surface, emerging with the energy,

$$\tfrac{1}{2}mv^2 = h\nu + E_k - W_a.$$

We have seen that at 0°K the electrons in the metal may have energies ranging from 0 up to a *sharply defined* maximum energy μ. Hence in the emergent electrons will be found a range of energies from 0 up to the maximum value given by,

$$\tfrac{1}{2}mv^2_{\max} = h\nu + \mu - W_a. \tag{6-38}$$

This is Einstein's equation. It will be noted that the Sommerfeld theory gives a definite physical reason for the existence *at low temperatures* of a sharply defined maximum emission energy. At high temperatures, however, there are an appreciable number of electrons having energies somewhat greater than μ; hence the maximum energy will in this case be less sharply defined.

It is evident from the above equation that the threshold frequency will be given by

$$h\nu_0 = W_a - \mu. \tag{6-39}$$

Hence we have at once the result that the photoelectric and thermionic work functions should be identical.

Since μ is independent of temperature, there will be, to a first approximation, no temperature dependence of ν_0, such as is predicted by the classical electron theory, owing to the thermal energy of the electrons. At higher temperatures, however, there will be some electrons with energies greater than μ, and hence there will be photoelectrons ejected by radiation of lower frequency than that given by Eq. (6-39). A detailed calculation of this temperature effect has recently been made by Fowler.[1]

6-23. Velocity Distribution of Photoelectrons.—This problem has been treated in a qualitative way by Fowler, who points out the fact that on the classical theories the presence of emission velocities less than the maximum was attributed to the energy losses due to scattering of the electrons as they pass through the metal on their way to the surface

[1] See Sec. 6-30.

(as in the theories of Thomson and Uspensky[1]). On the new theory scattering plays only a secondary rôle, since Sommerfeld has shown that the mean free path in this theory is sufficiently large (of the order of 100 atomic diameters) so that many of the electrons will reach the surface without collision. The velocity distribution of the emitted electrons will depend primarily, then, on the initial distribution within the metal.

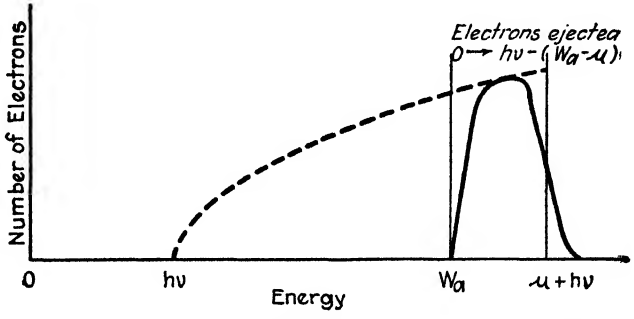

FIG. 6-14.—Energy distribution of photoelectrons. (*Fowler.*)

It is simplest to consider the *energy* distribution curve plotted in Fig. 6-13. If we assume that the chance that an electron will absorb a quantum is independent of its velocity, then the distribution of energy

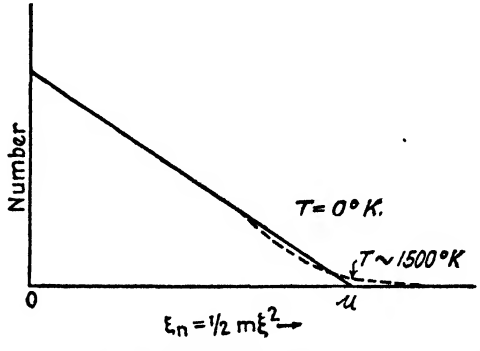

FIG. 6-15.—Distribution of energies normal to surface.

for the electrons which have already absorbed the energy $h\nu$ will be that shown by the dotted line in Fig. 6-14, covering a range from $h\nu$ to $h\nu + \mu$. Only the electrons which have a total energy greater than W_a will emerge; hence the distribution curve for these will be that of the curve to the right of W_a. Actually the curve will be rounded off slightly in the region of the maximum energy by the fact that this cut-off is not quite sharp, even at ordinary temperatures. Also some of the low-velocity electrons will be reflected back into the metal, so the actual curve to be expected will be of the form shown by the full line. This

[1] See Sec. 6-11 and 6-12.

curve resembles the experimental curves only in a general way, but this simple theory is incomplete in two respects. In the first place, Fig. 6-13 represents the distribution of the total energy of the electrons, while only the component normal to the surface is of interest. The curve referring only to this component has been given by Nordheim, and is of quite a different form (shown in Fig. 6-15). Furthermore, Wentzel has shown that the probability of absorption of a quantum is not independent of velocity, but is proportional to ξ, the component of velocity normal to the surface. The problem must therefore be considered anew along the lines laid down by Wentzel.

6-24. Theory of Wentzel.—Wentzel,[1] in an important paper, has recently laid the basis for a completely new theory of the photoelectric effect. The theory is based on the Sommerfeld conception of electrons in metals, and uses the methods of the wave mechanics in treating the interaction between light and electrons. It is a good illustration of the power of these new conceptions, and seems to offer the hope that ultimately a comprehensive, quantitative theory of the photoelectric effect may be developed.

Following the methods of the wave mechanics, the assembly of electrons within a block of metal may be treated as a system of standing waves, analogous to the electromagnetic waves in a *Hohlraum.* Such a system of waves ("Ψ-waves") can in general be represented by an expression of the form,[2]

$$\Psi_0 = A \sin\left(\frac{2\pi x}{\lambda_x}\right) \sin\left(\frac{2\pi y}{\lambda_y}\right) \sin\left(\frac{2\pi z}{\lambda_z}\right) \epsilon^{2\pi i \nu_e t}, \tag{6-40}$$

where λ_x, λ_y, λ_z are the x, y, and z components of the wave-length λ, so that,

$$\lambda_x^2 + \lambda_y^2 + \lambda_z^2 = \lambda^2.$$

If the block of metal has the dimensions l_1, l_2, l_3 along the x, y, z directions, respectively, the condition for standing waves is,

$$l_1 = \frac{n_1\lambda_x}{2},\ l_2 = \frac{n_2\lambda_y}{2},\ l_3 = \frac{n_3\lambda_z}{2},$$

where n_1, n_2, n_3 are integers. For the electrons we use the de Broglie relations,

$$\begin{aligned} \lambda &= \frac{h}{mv} = \frac{h}{(2W_0 m)^{\frac{1}{2}}} \\ \nu_e &= \frac{E}{h} = \frac{(mc^2 + W_0)}{h} \end{aligned} \tag{6-41}$$

where $W_0 = \frac{1}{2}mv^2$, v being the velocity of the electron.[3] Also we have,

[1] G. Wentzel, "Probleme der Modernen Physik," *Sommerfeld Festschrift*, p. 79.

[2] See L. Brillouin, "Les Statistiques Quantique," p. 244.

[3] This is equal to the *group* velocity of the wave.

$$\lambda_x = \frac{h}{mv_x}, \lambda_y = \frac{h}{mv_y}, \lambda_z = \frac{h}{mv_z}.$$

If we set

$$k_1 = \frac{2\pi}{\lambda_x}, k_2 = \frac{2\pi}{\lambda_y}, k_3 = \frac{2\pi}{\lambda_z}$$

so that

$$k_1^2 + k_2^2 + k_3^2 = k^2 = \frac{8\pi^2 m W_0}{h^2} = \frac{4\pi^2}{\lambda^2}, \tag{6-42}$$

then Eq. (6-40) becomes,

$$\Psi_0 = A \sin k_1 x \sin k_2 y \sin k_3 z \, \epsilon^{\left(\frac{2\pi i}{h}\right)Et}. \tag{6-43}$$

Let the face $x = 0$ of the metal block be illuminated by a beam of light of frequency ν. Within the metal then there will be an electromagnetic wave of the form,

$$E = E_0 \epsilon^{-\alpha x} \cos 2\pi[\nu t - (K \cdot r)], \tag{6-44}$$

where α is the absorption coefficient of the light in the metal and $K/2\pi$ the momentum vector ($= 1/\lambda$) of the radiation. The electron Ψ-waves will then be perturbed by this electromagnetic wave and Wentzel assumes that the perturbed wave function Ψ can be represented in the form

$$\Psi = \Psi_0 + \Psi_1,$$

where Ψ_0 is the unperturbed wave. Ψ_1 is then expanded in a Fourier series of the form,

$$\Psi_1 = \sum a \epsilon^{i(\kappa \cdot r) + \left(\frac{2\pi i}{h}\right)(mc^2 + W)t} \tag{6-45}$$

where $\kappa/2\pi$ = momentum vector of electron wave. The Fourier coefficients a are then calculated from the condition that Ψ must satisfy the Schroedinger equation, which for the case of a perturbing field which varies with the time, takes the form,

$$\left(\frac{h^2}{8\pi^2 m}\right)\nabla^2\Psi + \left(\frac{h}{2\pi i}\right)\frac{\partial \Psi}{\partial t} - mc^2\Psi = \left(\frac{eh}{8\pi^2 m\nu}\right)\epsilon^{-ax - i(K \cdot r) + 2\pi i \nu t}(E \text{ grad } \Psi). \tag{6-46}$$

Now the quantity $|\Psi_1|^2$, when integrated over the volume of the block, may be interpreted as the probability that an electron wave of kinetic energy W_0 will go over into an electron wave of energy W. Call this probability Z, then

$$Z = \int\int\int dxdydz|\Psi_1|^2. \tag{6-47}$$

The procedure is then to evaluate the coefficients a of Eq. (6-45) by substituting this expression for Ψ_1 in Eq. (6-46). The expression $|\Psi_1|^2$ can then be formed and substituted into the integrand of Eq. (6-47).

In carrying out the integration it is found that the integrand has appreciable values only in the case where $W = W_0 + h\nu$, that is, only when a complete quantum is absorbed by the electron wave. Carrying out the integration, Wentzel obtained the final result,

$$Z = \left(\frac{16\pi^3 mc^2}{l_1 h^3}\right)\left(\frac{h}{8\pi^2 m\nu}\right)^4 \left(\frac{k_1^2}{\kappa_x}\right)(E_x^2\kappa_x^2 + E_y^2 k_2^2 + E_z^2 k_3^2), \quad (6\text{–}48)$$

where

$$\kappa_x = \frac{2\pi m_1}{l_1},\ \kappa_y = \frac{2\pi m_2}{l_2},\ \kappa_z = \frac{2\pi m_3}{l_3};$$

$$m_1, m_2, m_3 = 1, 2, 3, \cdots;$$

and

$$W = \left(\frac{h^2}{8\pi^2 m}\right)\kappa^2 = \left(\frac{h^2}{8\pi^2 m}\right)(\kappa_x^2 + \kappa_y^2 + \kappa_z^2).$$

Equation (6-48) shows that Z varies as k_1^2/κ_x, that is, the probability of absorbing a quantum is greater for the electrons having the greatest momentum in a direction normal to the surface. To get I, the total photoelectric yield from the surface for light of frequency ν, the above expression must be summed over all values of the momenta of the electrons allowed by the Fermi distribution. There are three cases to be considered.

Case 1. $h\nu < (W_a - \mu)$.—If the energy of the incident light is less than the work function, then no electrons can absorb sufficient energy to escape and $I = 0$.

Case 2. $(W_a - \mu) < h\nu < W_a$.—In this case the integration is to be extended over all electrons for which $(W_0 + h\nu) \geqq W_a$. The result obtained is,

$$I = \frac{2e^2}{15\pi h^2}\left\{\nu^{-\frac{7}{2}}\left[\bar{\nu}^{\frac{5}{2}} - (\nu_a - \nu)^{\frac{5}{2}}\right]E_x^2 + \frac{\nu^{-\frac{3}{2}}}{14}\left[\bar{\nu}^{\frac{7}{2}} - (\nu_a - \nu)^{\frac{7}{2}}\right]\left[3E_x^2 + 2E_y^2 + 2E_z^2\right]\right\}, \quad (6\text{–}49)$$

where $h\bar{\nu} = \mu$, and $h\nu_a = W_a$.

This expression is the one of greatest physical interest, since the experimentally available frequencies almost invariably lie in this range.

Case 3. $h\nu > W_a$.—This condition will hold for most metals only for frequencies far in the ultra-violet. Obviously in this case the incident quantum has sufficient energy to eject any electron, even though its initial kinetic energy is zero. Consequently Z must be summed over all values of κ from zero up to the maximum. The final result in this case is,

$$I = \frac{2e^2}{15\pi h^2}\nu^{-\frac{7}{2}}\bar{\nu}^{\frac{5}{2}}\left[E_x^2 + \frac{1}{14}\frac{\bar{\nu}}{\nu}(3E_x^2 + 2E_y^2 + 2E_z^2)\right]. \quad (6\text{–}50)$$

The general characteristics of the spectral distribution predicted by Wentzel's theory can be seen from a study of Eq. (6-49). In the first place, it will be noted that I depends on two constants characteristic of the metal, ν_a and $\bar{\nu}$, or W_a and μ. Other theoretical expressions have depended only on the single parameter ν_0, which is proportional to the difference $(W_a - \mu)$. The theory thus allows a considerable divergence in the shape as well as the intercepts of the spectral distribution curves for different metals.

In the second place, it will be noted that I depends on the three components of the electrical intensity of the incident light, that is, on its polarization as well as the angle of incidence. We thus have the possibility that the theory will explain some of the puzzling features of polarization selectivity.

Wentzel did not make a comparison between his theory and experimental data, since he regarded the results as only qualitative, on account of the simplifying assumptions made. The theory has been presented in some detail here because it illustrates the general method by which the problem of photoelectric emission is attacked on the basis of the quantum mechanics. Houston[1] has recently pointed out that in integrating Eq. (6-48) over all electrons in the metal, Wentzel made use of the Fermi expression for the total energy of the electrons, while it is only their energy normal to the surface which determines whether or not they will be ejected. The probability function Z should therefore be integrated over the distribution represented in Fig. 6-15, rather than that of Fig. 6-13. When this correction is made Houston obtains the final result,

$$I = B\sqrt{\frac{\bar{\nu}}{\nu}}\left\{\frac{E_x^2}{\nu}\left[1 + \frac{\bar{\nu}}{2\nu}\right] + \frac{E_y^2 + E_z^2}{3\nu}\left[\frac{\nu - \nu_0}{\nu}\right]\right\}\left(\frac{\nu - \nu_0}{\nu}\right)^2,$$

where B is a constant. This expression has been plotted in Figs. 6-16 and 6-17 for the cases of potassium and silver and compared with typical experimental data for these metals obtained by Fleischer and Teichmann[2] and by Suhrmann,[3] respectively. In plotting the equation it was assumed that $E_y^2 + E_z^2 = 3E_x^2$, which would be true for unpolarized light incident at 45 deg. For this case the equation reduces to

$$I = BE_x^2\nu^{-\frac{3}{2}}(\nu - \nu_0)^2(2\nu + \tfrac{1}{2}\bar{\nu} - \nu_0).$$

The value of ν_0 was taken from the experimental data and $\bar{\nu}$ was computed from Eq. (6-32), assuming one free electron per atom for potassium and three for silver. It will be seen that the theory gives a curve which is of approximately the correct shape in the vicinity of the threshold, but at higher frequencies departs widely from the form of curve always obtained experimentally for the alkali metals.

[1] Quoted by E. O. Lawrence and L. B. Linford, *Phys. Rev.*, **36**, 482 (1930).

[2] R. Fleischer and H. Teichmann, *Zeits. f. Phys.*, **61**, 227 (1930).

[3] R. Suhrmann, *Zeits. f. Phys.*, **33**, 63 (1925).

6-25. Effects in Thin Films.—Fröhlich[1] has found that if the method used by Wentzel be applied to the problem of photoelectric effects in thin films of metal, the calculations can be carried out in more detail than for thick metal blocks, because of the simplification introduced by neglecting the effects of absorption of light and of electrons within the film. Following Wentzel, Fröhlich calculates the "eigen-functions" for an assembly of electrons within the metal, and then considers the perturbations

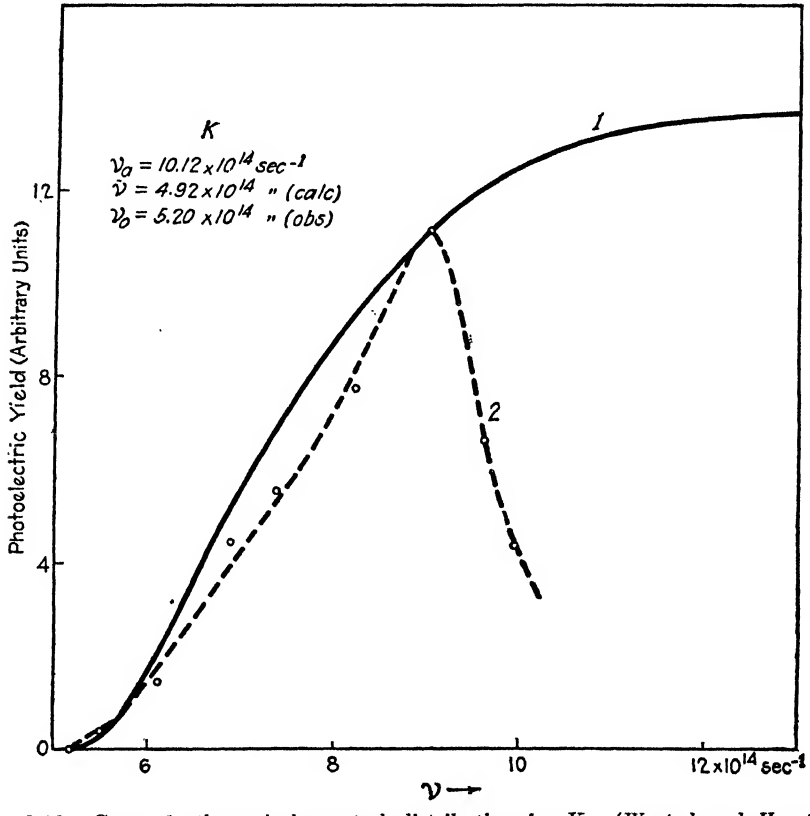

FIG. 6-16.—Curve 1, theoretical spectral distribution for K. (*Wentzel and Houston.*) Curve 2, experimental curve. (*Fleischer and Teichmann.*)

produced by a beam of radiation passing through the film. The actual magnitude of the photoelectric current, after a steady state has been reached, may be computed if it is assumed that the electrons obey the Fermi statistics and that the surface is perfectly plane. Since by a perfectly plane surface, in this case, is meant one whose irregularities are small compared to the de Broglie wave-length of the photoelectrons ($=h/mv$), it is evident that the theory will apply most accurately to the slow electrons ejected by low-frequency radiation, and hence in particular

[1] H. FRÖHLICH, *Ann. d. Phys.*, **7**, 103 (1930).

to those ejected from alkali metals by visible light of frequency not far from the threshold.

The magnitude of the photoelectric current excited by incident light of frequency ν turns out to be a complicated algebraic function of ν,

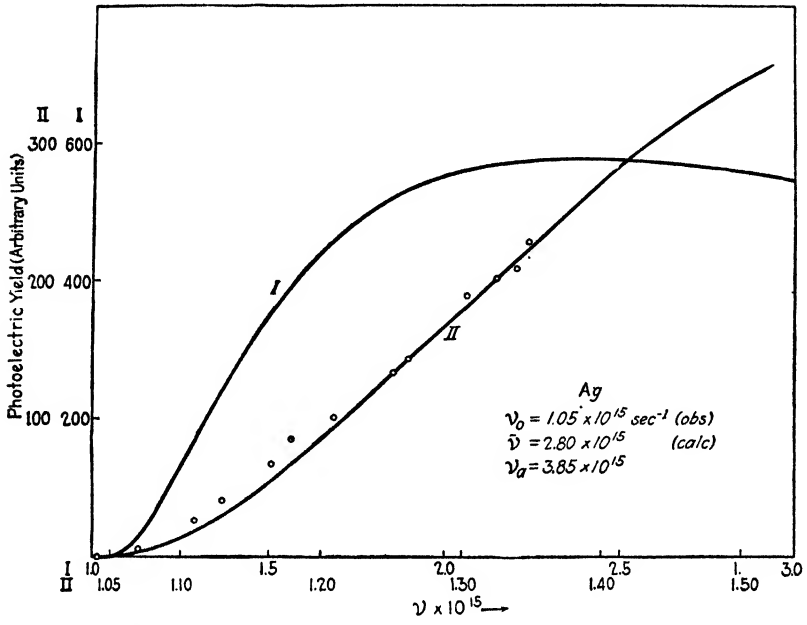

FIG. 6-17.—Theoretical spectral distribution for Ag (*Wentzel and Houston*) compared with experimental points of Suhrmann: I, complete curve (scale I); II, magnified portion near threshold (scale II).

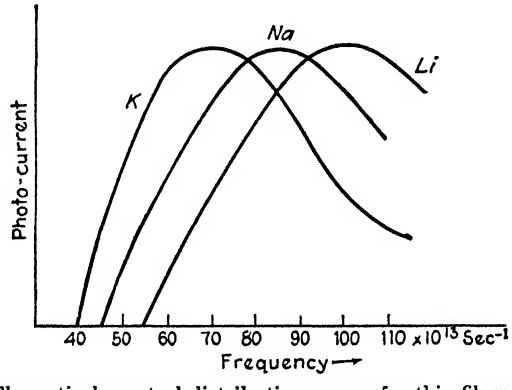

FIG. 6-18.—Theoretical spectral distribution curves for thin films. (*Fröhlich.*)

$\bar{\nu}$ and ν_a, where, as before, $\bar{\nu} = \mu/h$ and $\nu_a = W_a/h$. Calculating $\bar{\nu}$ by use of Eq. (6-32) and using experimental values for the threshold frequency ν_0 ($= [\nu_a - \bar{\nu}]$), Fröhlich obtained spectral distribution curves of the form shown in Fig. 6-18. It will be noted that the emission reaches

a maximum for values of ν ranging from 1.5 ν_0 to $2\nu_0$, as in the theories of Richardson and Thomson. No systematic experimental study of the spectral distribution curves for thin films of alkali metals has been made, so that the theory cannot be checked quantitatively. However, it can be seen that the general shape of the curves, particularly as regards the sharpness of the maximum, is similar to the experimental curves, and the positions of the maxima are in good agreement with the experimental results of Pohl and Pringsheim for thick layers of the alkali metals. Fröhlich shows that the positions of these maxima should not vary greatly with the film thickness, though the shapes of the curves would be expected to.

It turns out that the expression for the photoelectric current from a plane surface of a thin metal film depends only on that component of

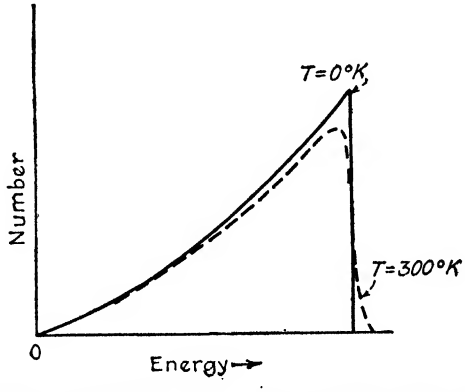

FIG. 6-19.—Theoretical energy distribution of photoelectrons from thin films. (*Fröhlich.*)

the electric vector of the incident light which is normal to the surface, and if this is zero the current should be zero. Such a surface should show a photoelectric effect, therefore, only for $E\|$ light.[1] Because of the irregularities in the surface, however, there will be an effect also for $E\perp$, and this effect will increase with increasing frequency of the incident light, since for higher frequencies the de Broglie wave-length of the electrons will be small. A large ratio of $I\|/I\perp$ should therefore be observed only for frequencies near the threshold, in agreement with experiments on polarization selectivity.

Fröhlich deduces also a quantitative expression for the energy distribution of the photoelectrons ejected from thin films, though the reader must again be referred to the original paper for the details of the calculations. The form of the distribution curve is shown in Fig. 6-19 for $T = 0°$ and $T = 300°$K, and in Fig. 6-20 the theoretical curve is compared with the experimental results of Lukirsky and Prilezaev[2] for

[1] See Chap. V. for an explanation of this notation.

[2] P. LUKIRSKY and S. PRILEZAEV, *Zeits. f. Phys.*, **49**, 236 (1928).

silver. It will be seen that as the thickness of the film is decreased, the energy-distribution curve approaches the form of the theoretical curve. The physical reason for the existence of the maximum in the curve just below the maximum energy is to be found in the fact that the probability of ejection is greater for electrons which already have a large velocity within the metal, so that high-velocity electrons should predominate. The change in shape of the curve observed for thicker films of metal is obviously due to the fact that most of the light is absorbed at some depth within the metal, and there is a general loss of energy of the electrons as they make their way to the surface; hence there is observed a relatively greater number of slow electrons. There will be deviations from the theoretical curve also, because actual surfaces are not perfectly plane to

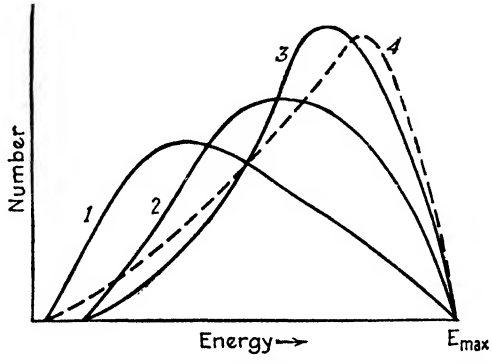

FIG. 6-20.—Energy distribution of photoelectrons from Ag. 1. Thick layer. 2. Film thickness, 3×10^{-6} cm. 3. 10^{-6} cm. (*Lukirsky and Prilezaev.*) 4. Theoretical curve. (*Fröhlich.*)

within one electron wave-length. (The de Broglie wave-length for an electron with a velocity of 1 volt is of the order of 10^{-7} cm.)

No quantitative calculations were made for the case of the heavier metals, since for these higher-velocity electrons are involved and the surface irregularities are of still greater importance. At least it is evident that for such metals the polarization selectivity (ratio of $I\|/I\perp$) should be considerably smaller than for alkali metals, and the maxima in the spectral distribution curves will in most cases occur too far in the ultraviolet to be observed. (For a silver film whose threshold is at 3000A a spectral maximum is predicted at 1600A.)[1]

6-26. Theory of Tamm and Schubin.—An important extension of the theory of the photoelectric effect has recently been made by Tamm and Schubin,[2] who make use of the idea that free electrons can absorb energy from the incident radiation only if they are in a force field which

[1] A further wave-mechanical treatment of the photoelectric effect in thin films has recently been given by W. G. PENNEY, *Proc. Roy. Soc.*, **133**, 407 (1931).

[2] I. TAMM and S. SCHUBIN, *Zeits. f. Phys.*, **68**, 97 (1931).

binds them to some sort of parent system. Hence only those electrons may be ejected which are in force fields of atoms within the metal, or in the work-function field outside the surface of the metal. They show that the latter electrons are responsible for the greater portion of the photoelectric emission from the metal for frequencies near the threshold, and it is only for considerably higher frequencies (of the order of twice the threshold frequency) that an appreciable number of electrons are ejected from within the metal.

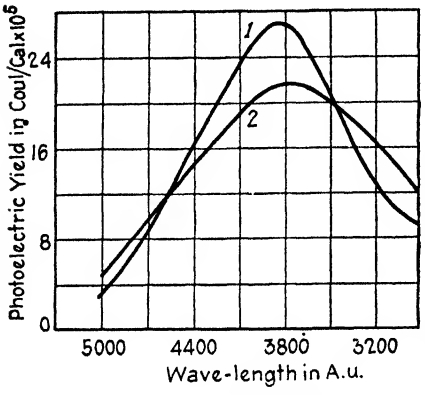

FIG. 6-21.—Spectral distribution curves for K. 1. Theoretical curve. (*Tamm and Schubin.*) 2. Experimental curve. (*Suhrmann and Theissing.*)

Writing down the Schroedinger equation for the electrons outside the metal surface, and considering the perturbations produced by the incident waves, they arrive at an expression for the photoelectric current as a function of the frequency which is similar to that derived by Fröhlich and which therefore yields spectral distribution curves of the proper shape. Their equation, however, allows them also to compute for the first time the numerical magnitude of the photoelectric current excited by unit intensity of incident light, and the results are in excellent agreement with those of Suhrmann and Theissing,[1] who measured the photoelectric yield from potassium in coulombs per calorie. The comparison of the theoretical and experimental curves is shown in Fig. 6-21. The equation given for the photoelectric current per unit intensity of light incident at an angle ϕ is,

$$I = \frac{e^2\nu_a}{2ch^2\nu^4 \cos\phi}\left(\frac{E_x^2}{E^2}\right)\left[S_1(\nu) + S_2(\nu)\right],$$

where E is the electric vector of the incident light, E_x its component perpendicular to the surface, and S_1 and S_2 stand for the integrals:

$$S_1 = 8\int_{\sqrt{\nu_a-\nu}}^{\sqrt{\bar{\nu}}} \frac{(\bar{\nu} - \xi^2)\xi^2 d\xi}{\sqrt{\xi^2 + \nu - \nu_a}},$$

$$S_2 = \frac{-\nu_a}{2}\int_{\sqrt{\nu_a-\nu}}^{\sqrt{\bar{\nu}}} \frac{(\bar{\nu} - \xi^2)\xi^2 d\xi}{(\xi^2 + \nu - \frac{16}{15}\nu_a)\sqrt{\xi^2 + \nu - \nu_a}}.$$

As before, $\nu_a = W_a/h$ and $\bar{\nu} = \mu/h$. For $\nu > \nu_a$, the lower limit of each integral is zero.

[1] R. SUHRMANN and H. THEISSING, *Zeits. f. Phys.*, **52**, 453 (1928).

In treating the ejection of photoelectrons from *within* the metal, Tamm and Schubin make use of a diffraction condition derived by Kronig,[1] which states that the momentum vector, $2\pi/\lambda$, of the electron waves within the metal can be increased or decreased only by whole multiples of a quantity, $2\pi/a$, where a is the distance between planes in the crystal. It then turns out that electrons can absorb the necessary momentum, and at the same time attain enough energy to escape from the metal, only when the incident frequency is greater than a certain value ν_0', which they call the second threshold. For potassium, for which λ_0 is 6200A, λ_0' turns out to be 3850A. For shorter wave-lengths than this the volume effect rises rapidly, and this accounts, they believe, for the rise in the spectral distribution curve sometimes observed on the short wave-length side of the selective maximum.

6-27. The Surface Work Function.—It has already been pointed out that one of the most striking consequences of the Sommerfeld theory is that the work function of a metal surface is interpreted as the difference between the surface potential jump W_a and the internal potential of the electrons, μ. Since the latter quantity for most metals is of the order of 10 volts, the electrostatic potential jump through the surface must be of the order of 15 volts (varying from 10 to 25 volts for different metals). At the time the theory was published there existed no experimental evidence for potential differences of such a magnitude at metal surfaces—it being generally assumed that the potential jumps were of the order of magnitude of ϕ, *i.e.*, approximately 5 volts. On the other hand, there were no experiments which denied the existence of much larger potential differences, and it seemed that there could be no experimental test of this point of the theory. However, almost simultaneously with the publication of the Sommerfeld theory, late in 1927, Davisson and Germer[2] announced the results of their remarkable experiments on the diffraction of electrons by nickel crystals—and these experiments, when properly interpreted, were found to yield a direct confirmation of the Sommerfeld view of surface potentials.

It will be remembered that Davisson and Germer found that the directions of the electron beams diffracted by the *space* lattice (as distinguished from the *plane grating* beams) could not be predicted by assigning to the electrons the wave-length given by the de Broglie relation, $\lambda = h/mv$. Instead it was necessary either to assume a contraction of the crystal lattice or else to assign to the electrons a smaller wave-length λ'. The interpretation of this apparent discrepancy was given by Rosenfeld and Witmer,[3] and Bethe.[4] They pointed out that, on entering

[1] R. DE L. KRONIG, *Proc. Roy. Soc.*, **124**, 409 (1929).
[2] C. DAVISSON and L. H. GERMER, *Phys. Rev.*, **30**, 705 (1927).
[3] L. ROSENFELD and E. E. WITMER, *Zeits. f. Phys.*, **49**, 534 (1928).
[4] H. BETHE, *Ann. d. Phys.*, **87**, 55 (1928).

the crystal, the electron waves would be refracted and hence would suffer a change in wave-length such that $\lambda' = \lambda/\beta$, where β is an "index of refraction." β can be calculated from Davisson and Germer's data and comes out to be a number greater than unity. This means that the electrons must be speeded up as they enter the metal. But this is just what we would expect if they fall through a surface potential jump, W_a. For example, let a beam of electrons approach a metal surface after having been accelerated through a potential V. The de Broglie wave-length then will be,

$$\lambda = \frac{h}{mv} = \frac{h}{\sqrt{2meV}}.$$

On passing through the surface the electron is accelerated through the potential W_a, so that the new wave-length is

$$\lambda' = \frac{h}{\sqrt{2me(V + W_a)}},$$

so that the effective index of refraction is,

$$\beta = \frac{\lambda}{\lambda'} = \sqrt{1 + \frac{W_a}{V}}.$$

Since β and V are determined experimentally, we can calculate W_a. The question is, then, are the calculated values of W_a of the order of 2 to 5 volts as demanded by the older theory, or of the order of 10 to 25 volts, as demanded by the Sommerfeld theory? The answer is decisively in favor of the Sommerfeld theory—the values obtained for nickel being very close to 15 volts. Other observers[1] have obtained similar values for several other metals, so that the electron diffraction experiments strikingly confirm the Sommerfeld view.

We tabulate below values of W_a obtained from diffraction experiments, together with the values of μ for the corresponding metal, calculated from Eq. (6-32), and the values of the work function obtained from the relation,

$$\phi = W_a - \mu.$$

Considering the errors of the electron diffraction experiments (which usually give a value of W_a uncertain to ± 5 volts), the agreement with the directly observed values of the work function, which range between 4 and 5 volts for these metals, is quite satisfactory.

[1] E. Rupp, *Ann. d. Phys.*, **85**, 981 (1928); an excellent summary of all the work in this field will be found in G. P. Thomson, "The Wave Mechanics of Free Electrons," (McGraw-Hill Book Company, Inc., 1930).

TABLE 6-1*.—VALUES OF SOMMERFELD WORK FUNCTIONS

	Al	Cr	Ni	Cu	Ag	Au	Pb
W_a (observed), volts	18	20	18	17	18	17	11
μ (calculated), volts	11.6	13.9	15.3	11.2	11.5	11.5	7.8
η	3	3	3	2	3	3	3
$W_a - \mu$, volts	6.4	6.1	2.7	5.8	6.5	5.5	3.2

* Taken from L. Rosenfeld and E. E. Witmer, *loc. cit.*

There is an uncertainty in the calculations of μ as to what value of η, the number of free electrons per atom, to assume. The values of η assumed in calculating the above table are given in the third row, and it is surprising that in order to give values of $W_a - \mu$ which are of the same order of magnitude as the work function, it is necessary to assume η to be as large as 3. It is probably unprofitable to discuss this point further until more accurate measurements of W_a can be made.

6-28. Transmission of Electrons through Potential Barriers.—In all theories of photoelectric and thermionic emission it has been assumed that *all* electrons which come up to the surface from within with sufficient kinetic energy normal to the surface to surmount the potential barrier

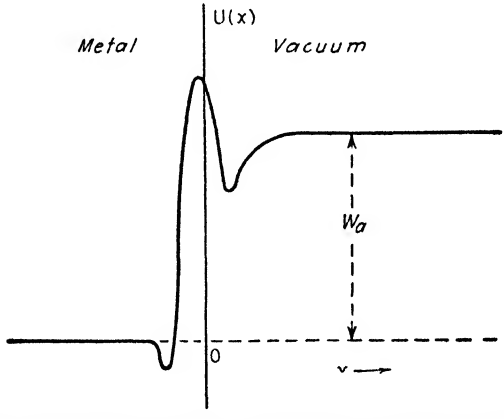

FIG. 6-22.—Hypothetical variation of potential energy at a metal surface.

would escape, while all those with smaller energies would be reflected back into the metal. This is a problem which can be treated on the basis of the quantum mechanics, and Fowler and Nordheim[1] have shown that the above assumption is true only in certain very special cases, while in other cases it may be far from the truth. The problem is treated theoretically under the head of One-dimensional Collisions, and the quantum theory of such collisions has recently been reviewed by

[1] R. H. FOWLER and L. NORDHEIM, *Proc. Roy. Soc.*, **119**, 173 (1928).

Nordheim[1] and by Condon.[2] We shall simply state a few of the results for important special cases.

Let $U(x)$ represent the potential energy of an electron in the vicinity of a metal surface which coincides with the plane $x = 0$. We assume that for large negative values of x (within the metal) the potential energy is constant and equal to zero; while for large positive values of x the energy reaches the constant value W_a. In the immediate vicinity of $x = 0$, U may vary in an arbitrary manner, so that the function may be of the type shown in Fig. 6-22. We now allow an infinite plane de Broglie wave—a beam of electrons—to approach the surface from within the metal with the energy W. When a steady state has been reached the

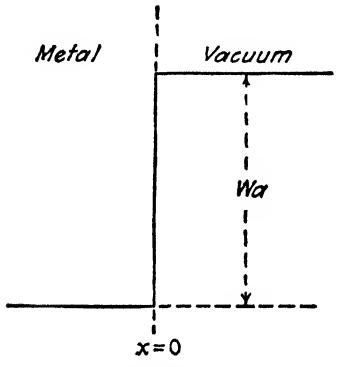

FIG. 6-23.—Ideal surface potential barrier.

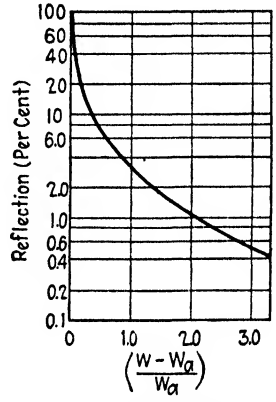

FIG. 6-24.—Reflection coefficient of electrons of energy W at the potential barrier of Fig. 6-23.

charge distribution and the current may be obtained by seeking a solution of the Schroedinger equation,

$$\nabla^2\Psi + \left(\frac{8\pi^2 m}{h^2}\right)(W - U)\Psi = 0. \tag{6-51}$$

For large positive or negative values of x the solution will be exponential in form and the squares of the amplitudes of the exponential functions will be proportional to the intensity of the electron waves, and hence to the current density. Thus for large negative values of x there will be two terms in the solution, one representing an electron wave traveling in the positive direction of x—the incident wave; and the other representing a wave proceeding in the negative direction—the reflected wave. The ratio of intensities of the reflected to the incident wave is the reflection coefficient R of the surface. For large positive values of x there is but one exponential term, representing the transmitted wave, and the

[1] L. NORDHEIM, *Phys. Zeits.*, **30**, 177 (1929).
[2] E. U. CONDON, *Rev. Mod. Phys.*, **3**, 43 (1931).

ratio of its intensity to that of the incident wave is the transmission coefficient D. Obviously we must have the condition $D + R = 1$.

The Schroedinger equation has been solved and the transmission coefficients calculated only for certain simplified forms of the potential

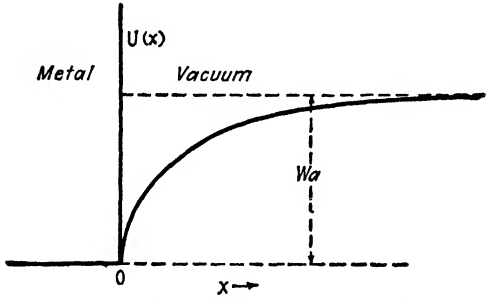

FIG. 6-25.—Potential barrier for an image field.

function $U(x)$. The simplest case is the one in which the potential energy jumps suddenly from 0 to W_a at the point $x = 0$, as shown in Fig. 6-23. For this case it is found that $R = 1$ and $D = 0$ for W less than W_a, as would be expected. For W greater than W_a, however, the reflection coefficient is given by the expression,

$$R = \left(\frac{1 - \sqrt{1 - \frac{W_a}{W}}}{1 + \sqrt{1 - \frac{W_a}{W}}} \right)^2.$$

In Fig. 6-24, taken from Condon's paper, R is plotted as a function of $(W - W_a)/W_a$. It is evident that $R = 1$ and hence $D = 0$ for $W = W_a$, and R drops rapidly to zero for larger values of W. However, in photoelectric experiments, the velocities of the emitted electrons seldom exceed 1 volt, while $W_a \sim 15$ volts. Hence $(W - W_a)/W_a = \frac{1}{15}$, and from the curve, $R = 0.4$ and $D = 0.6$. The *average* transmission coefficient for photoelectrons would thus be of the order of $\frac{1}{2}$ or less. A similar conclusion would apply to thermionic electrons.

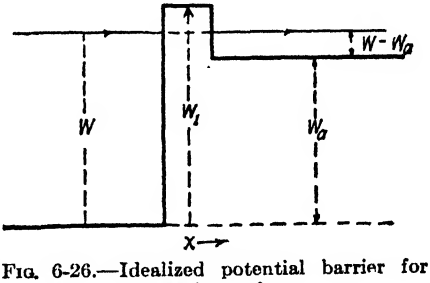

FIG. 6-26.—Idealized potential barrier for composite surface.

Somewhat larger transmission coefficients are obtained if the potential barrier is of the form shown in Fig. 6-25, which represents the potential due to an image force. The calculations for this case have been worked out in detail by Nordheim, who finds that $D = 0.93$ for $W = W_a$, with a rapid increase to unity for larger values of W.

The results are more striking for potential variations of the type shown in Fig. 6-26. Such a variation might be caused, for example, by the combined action of an image force and a surface double layer. On the classical theory only those electrons could escape for which W is greater than the maximum value W_1, and the work function would therefore be equal to W_1. On the present theory, however, if the "hump" is not too high or too broad, a certain fraction of the electrons with energies between W_a and W_1 will filter through with a net energy loss of W_a. The work function then will be equal to W_a rather than to W_1. This phenomenon is analogous to the familiar fact in optics that light waves may pass from glass into air and into another piece of glass—*even at angles greater than that of total internal reflection*—providing the intervening air film is sufficiently thin.

The presence of such a hill in the potential-energy curves will result in a reduced transmission coefficient for electrons of energy between W_a and W_1. The exact values of D and R have been worked out for this case and the detailed results and curves given by Nordheim and Condon. It is of interest to note that the transmission coefficient D does not increase continuously as W increases beyond W_a, but shows in the region $W_a < W < W_1$ a series of maxima and minima. This is due to a sort of interference phenomenon as the electron waves pass through the hill. A somewhat similar phenomenon for more complex potential barriers is discussed in Sec. 6-29.

The presence of a hill in the potential energy curve for a metal surface would give rise to two important experimental results. In the first place, in the photoelectric effect the hill would serve to filter out some of the low-velocity electrons and greatly reduce the photoelectric yield, particularly for frequencies close to the threshold. Any complete theory of the velocity or spectral distribution functions would have to take into consideration this possibility.

In the second place, as we have seen, Fowler and Nordheim have shown that the average transmission coefficient $\bar{D}$ for electrons of energy greater than W_a enters as a factor in the thermionic equation, which then takes the form,

$$I = AT^2\bar{D}\epsilon^{\frac{-(W_a - \mu)}{kT}}.$$

The effect of this factor would be to reduce the observed value of the constant A. There is good evidence that for coated surfaces this coefficient has values much smaller than the theoretical value 120 given by the Sommerfeld theory. For thoriated-tungsten surfaces, for example, the measured value of A is but 3 amp/cm^2 deg^2. This would be at once explained on the present theory as due to a potential hump at the surface, whose average transmission coefficient for electrons was only $\frac{1}{40}$. The

low observed values of A for coated surfaces might then be taken as experimental evidence that the potential variation through such surfaces is of the type shown in Fig. 6-26. Furthermore, if $W_1 - W_a$ is interpreted as the decrease in the surface work function due to a surface layer, this theory explains why small values of A always accompany small values of b_0. Since no method has as yet been discovered for determining directly the nature of surface potential variations, it is not certain how much physical significance can be attached to the particular types which have been assumed.

A surface potential hill of the type shown in Fig. 6-27 has found an important application in the theory of the "cold discharge" in intense

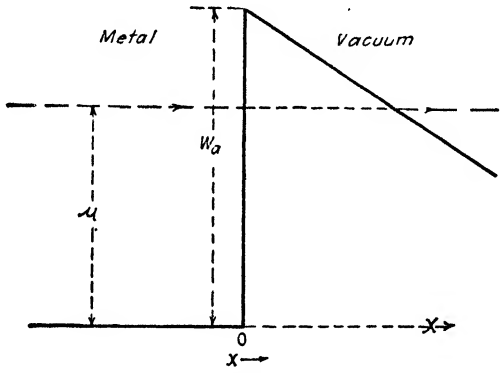

FIG. 6-27.—Potential barrier modified by an applied field.

electric fields. On the classical theory only those electrons can escape which can surmount the peak of the potential barrier—and the number of such electrons would show a strong temperature dependence. The field currents are, however, independent of temperature. On the present theory they are attributed to transitions of electrons *through* the barrier, and this assumption yields results in good agreement with experiment.[1]

6-29. Selective Transmission.—An interesting extension of the theory of transmission of electrons through potential barriers has recently been made by Campbell[2] and Fowler.[3] Campbell reviews the experimental evidence which points to the fact that many surfaces which show marked spectral selectivity are composite surfaces of some type, *e.g.*, "sensitized" potassium, thin-film caesium, surfaces coated with gas layers, etc. He points out that in most cases these surfaces probably consist of a thin film of sensitive alkali metal deposited on a layer of

[1] R. H. FOWLER and L. NORDHEIM, *loc. cit.*, and J. R. OPPENHEIMER, *Phys. Rev.*, **31**, 66 (1928).

[2] N. R. CAMPBELL, "Photoelectric Cells and Their Applications," *Discussion of the Physical and Optical Societies of London*, p. 10 (1930).

[3] R. H. FOWLER, *Proc. Roy. Soc.*, **128**, 123 (1930).

electronegative material, *e.g.*, oxygen, which in turn is supported by the base metal. The intermediate electronegative material plays an important rôle as a binding material. Campbell concludes that it is reasonable to expect that the potential variations through such a composite surface would be of the type shown in an idealized form in Fig. 6-28.

Granting this to be the case, Fowler has shown that a surface of this type has the property of transmitting selectively electrons coming up from within, with velocities in a certain restricted range. On inserting a potential function of this type in the Schroedinger wave equation, Fowler obtained the expression for the transmission coefficient as a function of the energy W of the impinging electrons. As would be

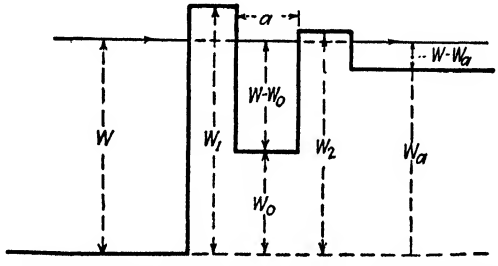

FIG. 6-28.—Potential barrier showing selective transmission.

expected, this equation gives $D = 0$ for $W < W_a$ and $D = 1$ for $W \gg W_1$. For values of W between W_a and W_1 the transmission coefficient is very small, except for certain critical values of W for which D shows a pronounced maximum. These values of W are such that the electron waves, after penetrating into the valley with a net energy loss W_0, have just the right de Broglie wave-length to form standing waves in the valley.

Since the de Broglie wave-length of an electron of energy $(W - W_0)$ is given by

$$\lambda = \frac{h}{mv} = \frac{h}{\sqrt{2m(W - W_0)}}, \tag{6-52}$$

the condition for selective transmission is

$$\frac{1}{2}n\lambda = \frac{nh}{2\sqrt{2m(W - W_0)}} = a,$$

where n is an integer and a the width of the valley.

It will be noted that this condition will be satisfied by a series of values of W, but Fowler shows that usually only one of these will fall in the range $W_0 < W < W_2$ in which standing waves may be formed. In case, however, the valley is very deep (W_0 small) there may be two critical values of W.

The energy of the photoelectrons coming up from within the metal is

$$W = E_k + h\nu,$$

where E_k is the kinetic energy determined from the Fermi statistics and ν the frequency of the incident radiation. Hence there will be a certain critical value (or possibly two values) of the incident *frequency* for which the surface will show a large transmission, and this will give rise to a selective maximum in the spectral distribution curve. If, as seems reasonable, it is assumed that the initial impulse given to the photoelectron is in the direction of the electric vector, then the selective maximum will be pronounced only for $E\|$ light which has a component normal to the surface, and for which the electrons can approach the surface normally without first undergoing collisions.

The chief features of the selective photoelectric effect thus find at least a qualitative explanation on the basis of this theory. It is uncertain again how much physical significance can be attached to the assumption of potential variations of this type, though Olpin[1] has recently reported a remarkable quantitative agreement between the values of the width of the potential valley determined from the positions of the selective maxima for various composite surfaces, and the values arrived at from a knowledge of the structure of the surface layers.

Whether or not Fowler's theory turns out to have quantitative significance, it is consistent with the fact that spectral selectivity depends greatly on the surface structure. The idea of a surface having a selective transmission for electrons comes out quite naturally in the quantum mechanics, though it is quite foreign to any classical electron theory. Certainly some type of selective transmission by the surface seems to be a most natural explanation of spectral selectivity, and when this idea is combined with the theories of Wentzel and Fröhlich it may lead to results in more exact agreement with experiment.[2]

6-30. Effect of Temperature.—Very recently the effect of temperature on photoelectric emission has been treated in detail by R. H. Fowler[3] on the basis of the Sommerfeld theory. It will be remembered that the energy distribution curve for electrons obeying the Fermi statistics is almost unaffected by temperature, except in the vicinity of the maximum energy. (Fig. 6-13.) It has therefore usually been assumed that the photoelectric effect would show no appreciable dependence on temperature except at very high temperatures. Fowler's treatment, however, brings out the fact that when electrons are ejected by light of *frequency*

[1] A. R. Olpin, *Phys. Rev.*, **37**, 465 (1931); **38**, 1745 (1931).

[2] See however the note to Sec. **5-15**, page 184.

[3] The authors are greatly indebted to Prof. C. E. Mendenhall who informed them of Professor Fowler's work, and to Professor Fowler for furnishing a copy of his manuscript, which has since been published (*Phys. Rev.*, **38**, 45 [1931].

near the threshold it is *only* the electrons of maximum energy which are available for ejection, and the effect of temperature on these is of considerable importance. It turns out, in fact, that for all temperatures above 0°K the spectral distribution curves should show an asymptotic approach to the frequency axis so that the term "threshold" as usually defined loses quantitative significance. This asymptotic approach, particularly at higher temperatures, is just the effect which has been observed in the careful experiments of Morris, Winch, and Cardwell; and Fowler's theory accounts quantitatively for these results. Furthermore, the theory gives a method by which the experimental results may be analyzed in order to determine the *true* photoelectric threshold. The true threshold ν_0 is defined from the equation[1]

$$h\nu_0 = W_a - \mu,$$

and may be contrasted with the *apparent* threshold which is obtained by the ordinary method of extrapolating the spectral distribution curves. The latter method would give the true threshold only if the measurements were made at the absolute zero.

Fowler proceeds to compute the number of electrons which will be ejected from a surface at the temperature T by light of frequency ν which is close to ν_0. He assumes that this number will be proportional to N_B, the number of electrons per unit volume within the metal which have a velocity component ξ normal to the surface which is greater than the critical value ξ_0, such that

$$\tfrac{1}{2}m\xi_0^2 + h\nu = W_a.$$

N_B is called the number of *available* electrons and is simply the number with energies normal to the surface such that after absorbing the additional energy $h\nu$ they will be able to surmount the surface potential barrier W_a. If $n(\xi)d\xi$ is the number of electrons per unit volume having normal velocity components in the range $d\xi$, then

$$N_B = \int_{\xi_0}^{\infty} n(\xi)d\xi.$$

As pointed out in Sec. **6-21**, $n(\xi)d\xi$ may be obtained by integrating Eq. 6-29 with respect to η and ζ from $-\infty$ to $+\infty$. The result is,

$$n(\xi)d\xi = \frac{4\pi kTm^2}{h^3} \log\left(1 + e^{\frac{\mu - \frac{1}{2}m\xi^2}{kT}}\right)d\xi.$$

The curve of $n(\xi)$ as a function of ξ^2 has already been shown in Fig. 6-15. By making approximations which are valid in case ν is not very different from ν_0, the logarithm may be expanded and integrated term by term.

[1] Fowler's notation has been modified in this equation and in those that follow in order to conform with that used in the previous sections of this chapter.

Writing $\phi = W_a - \mu = h\nu_0$ and setting $x = (h\nu - \phi)/kT = h(\nu - \nu_0)/kT$, the results obtained are,

$$N_B = \frac{2\sqrt{2}\pi m^{\frac{3}{2}}k^2T^2}{h^3(W_a - h\nu)^{\frac{1}{2}}}\left(e^x - \frac{e^{2x}}{2^2} + \frac{e^{3x}}{3^2} \cdots\right)$$

for $x \gtrless 0$, and

$$N_B = \frac{2\sqrt{2}\pi m^{\frac{3}{2}}k^2T^2}{h^3(W_a - h\nu)^{\frac{1}{2}}}\left[\frac{\pi^2}{6} + \frac{x^2}{2} - \left(e^{-x} - \frac{e^{-2x}}{2^2} + \frac{e^{-3x}}{3^2} \cdots\right)\right]$$

for $x \gtrless 0$.

It is evident that there will actually be a photoelectric emission for $\nu < \nu_0$ ($x < 0$), except in the limit as T approaches zero when the above expressions reduce to

$$N_B = 0, \text{ for } x \gtrless 0 \ (i.e., \ \nu < \nu_0),$$

$$N_B \sim \frac{[h(\nu - \nu_0)]^2}{(W_a - h\nu)^{\frac{1}{2}}}, \text{ for } x \gtrless 0 \ (i.e., \ \nu > \nu_0).$$

At $h\nu = \phi$ (*i.e.*, $\nu = \nu_0$) it is seen that N_B is proportional to T^2.

Making use of the assumption that the photoelectric emission I is proportional to N_B it is seen that we may write

$$I = AT^2(W_a - h\nu)^{-\frac{1}{2}}f(x), \tag{6-53}$$

or

$$\frac{I}{T^2} = A(W_a - h\nu)^{-\frac{1}{2}}f(x) = A(W_a - h\nu)^{-\frac{1}{2}}f\left(\frac{h(\nu - \nu_0)}{kT}\right),$$

where A is a constant and

$$\begin{aligned} f(x) &= e^x - \frac{e^{2x}}{2^2} + \frac{e^{3x}}{3^2} - \cdots, \ x \gtrless 0, \\ f(x) &= \frac{\pi^2}{6} + \frac{x^2}{2} - \left(e^{-x} - \frac{e^{-2x}}{2^2} + \frac{e^{-3x}}{3^2} - \cdots\right), \ x \gtrless 0. \end{aligned} \tag{6-54}$$

$f(x)$ is thus a universal function of x, whose form is the same for all metals and all temperatures.

Furthermore, it turns out that for frequencies near ν_0 the quantity $(W_a - h\nu)^{\frac{1}{2}}$ is practically a constant and may be included with the factor A. Taking logarithms we have then

$$\log\left(\frac{I}{T^2}\right) = B + F(x), \tag{6-55}$$

where B is a new constant independent of ν and T, and $F(x) = \log f(x)$. The theoretical curve $F(x)$ may at once be plotted as a function of x. Now, if the observed values of the photoelectric yield I are plotted in the form $\log (I/T^2)$ as a function of $h\nu/kT$, it is seen that if the observed curve is shifted horizontally by an amount ϕ/kT and vertically by an amount B it should coincide with the theoretical curve, and this should be true for any metal and for any temperature. The amount of the verti-

cal shift is unimportant but, for a given metal, should be the same for all temperatures. The horizontal shift required to bring about the coincidence, however, determines ϕ and hence ν_0, the true threshold. The form of the theoretical curve and the method of shifting the observed curves are indicated in Fig. 6-29.

Fowler has analyzed the experimental results for Ag, Au, Ta, Sn, and K, obtained in the careful experiments of Winch, Morris, Cardwell, Goetz, and Lawrence and Linford, respectively, and finds in all cases an excellent agreement with the above predictions. The results for silver and gold are shown in Figs. 6-30 and 6-31, in which experimental

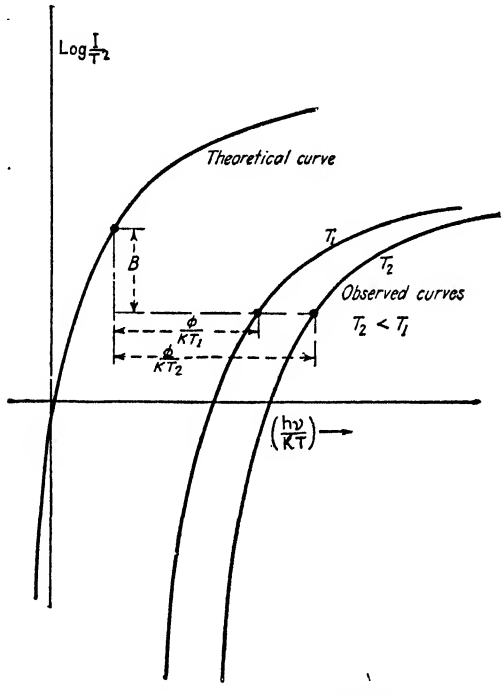

FIG. 6-29.—Fowler's method of determining the *true* photoelectric threshold.

points for three different temperatures have been plotted. All points for each metal have been shifted vertically by the same amount, and from the horizontal shift required for each temperature the work function determined. The results for Ag, Au, and Ta are tabulated (Table 6-2, p. 247). The second column gives the magnitude of the horizontal shift which is equal to ϕ/kT, ϕ being the true work function. The third and fourth columns show the values of ϕ and the corresponding values of the true threshold wave-length λ_0. In the last column have been listed for comparison the values of the apparent threshold, obtained by the method of extrapolating the spectral distribution curves.

The agreement with the experimental curve is well within experimental error and it is seen that the value of the true threshold obtained is independent of the temperature at which the measurements were taken.

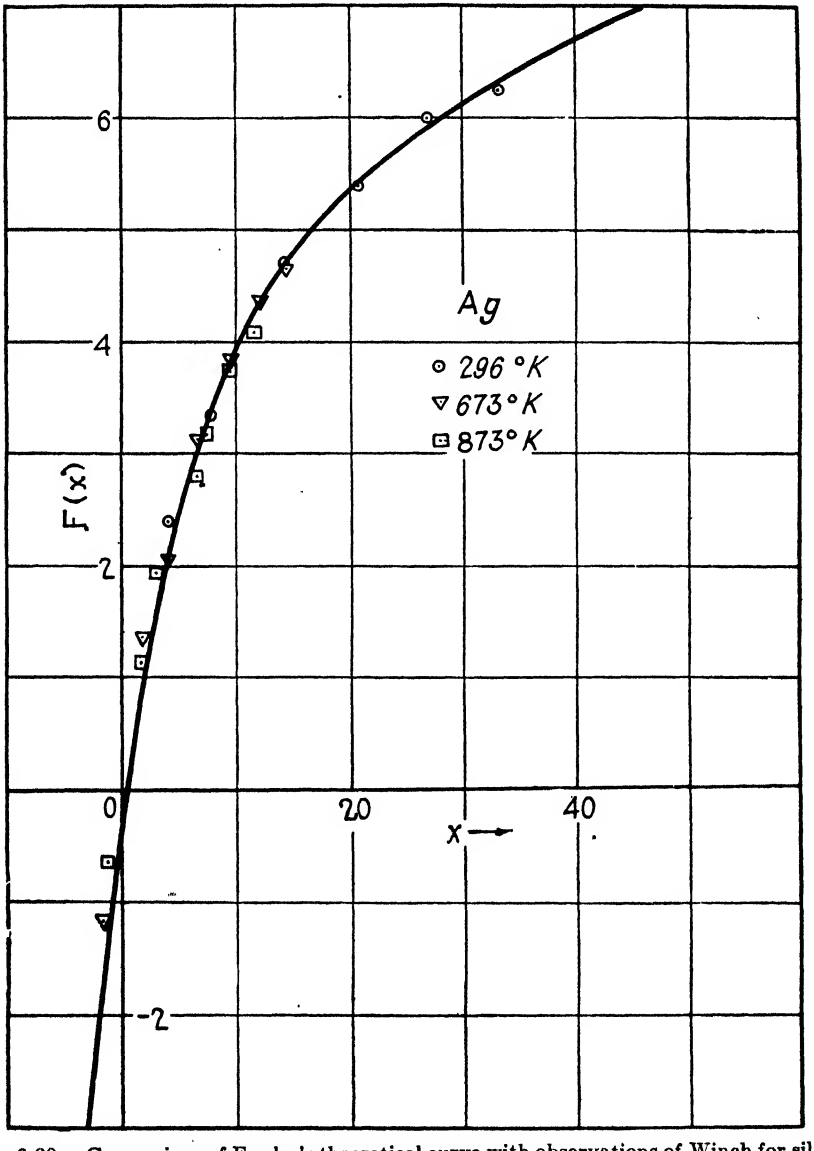

FIG. 6-30.—Comparison of Fowler's theoretical curve with observations of Winch for silver.

The values of the apparent thresholds change by as much as 100A over this temperature range and differ from the true thresholds by as much as 160A. The effect of temperature is thus by no means negligible, even at room temperature.

These results are of the greatest interest and importance, since they give for the first time a satisfactory theory of the effect of temperature on photoelectric emission and at the same time furnish a new method of

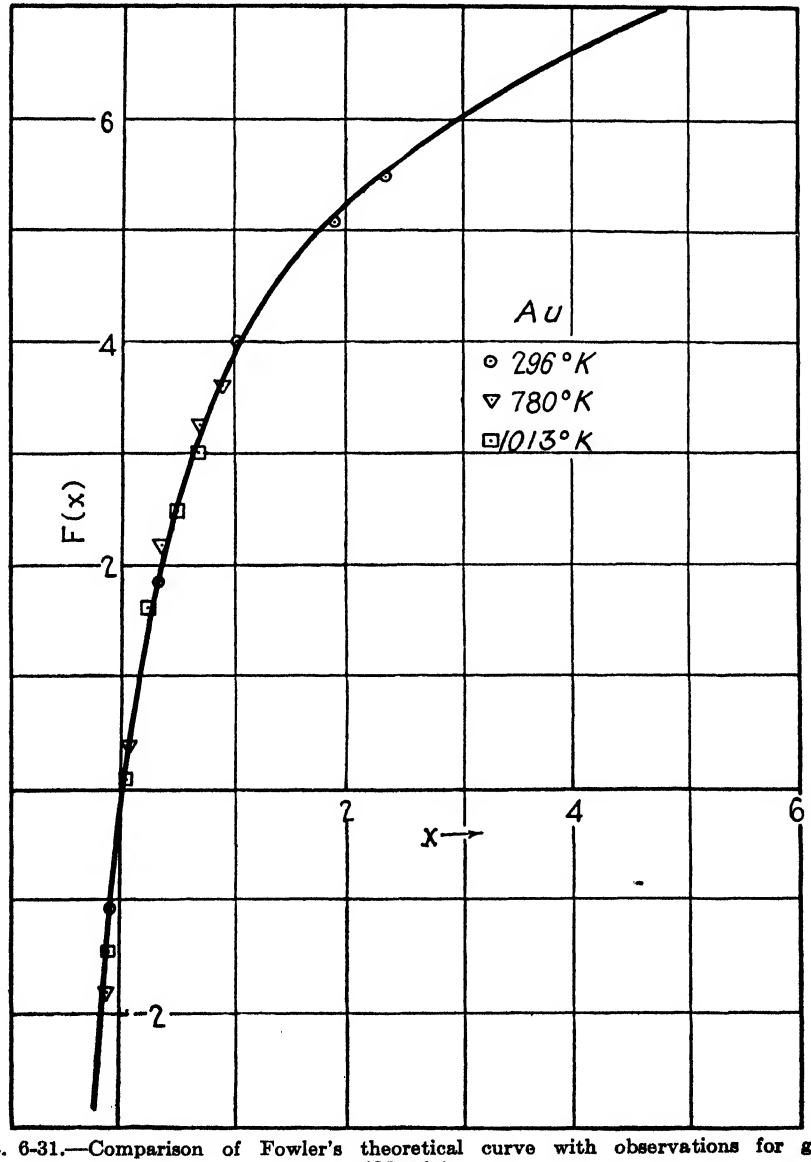

FIG. 6-31.—Comparison of Fowler's theoretical curve with observations for gold. (*Morris.*)

analysis of experimental data which should be of great power and usefulness. They bring out also the fact that the phrase, "temperature dependence of ν_0," probably has no definite meaning since ν_0 is not defined for

TABLE 6-2.—DETERMINATION OF THE TRUE PHOTOELECTRIC THRESHOLD

°K	ϕ/kT (from curves)	ϕ, volts	λ_0 (true)	λ_0 (apparent)
		Silver		
296	184.8	4.71	2620	2610
673	82.2	4.76	2592	
873	63.3	4.75	2590	2700
		Mean 4.74	2603	
		Gold		
296	191.0	4.86	2530	2650
733	78.0	4.92	2500	
1013	56.5	4.92	2500	2610
		Mean 4.90	2510	
		Tantalum		
293	162.5	4.10	3010	3050
973	49.5	4.14	2970	3150
		Mean 4.12	2990	

any temperature above 0°K. The agreement with experiment supplies also a convincing direct test for the validity of the Fermi statistics as applied to electrons within the metal.[1]

For the convenience of those wishing to make an accurate plot of the Fowler theoretical function we have tabulated in Table 6-3 the values of the function $F(x)$ for a series of values of x, computed from Eq. (6-54).

Since the above was written one of the authors[2] has made a further experimental test of Fowler's theory, applying it to new photoelectric data for clean palladium. Measurements of I as a function of ν were made for 8 different temperatures lying in the range 300 to 1070°K, and all of the observed curves were found, after shifting, to fall accurately on the theoretical curve. The values of the true work function deduced from the eight curves all agree with each other within 0.02 volt, the mean value being 4.97 volts.

[1] Fowler has also used a somewhat more exact method of computing the photoelectric yield in which he includes the transmission probability of the electrons through the surface potential barrier. This leads to an equation quite similar to Eq. 6-55 except that T^2 is replaced by $T^{\frac{3}{2}}$ and $F(x)$ has a somewhat different form. The theoretical curve obtained is however quite similar to that obtained by the simpler method and experiments are scarcely able to decide between the two. Quite recently L. A. Young and N. H. Frank have proposed a modification in which the factor $T^{\frac{3}{2}}$ appears, but no attempt has been made to fit this to the experimental data (*Phys. Rev.*, **38**, 838 [1931]).

[2] L. A. DuBridge and W. W. Roehr, *Phys. Rev.*, Jan. 1, 1932; L. A. DuBridge, *Phys. Rev.*, Jan. 1, 1932.

TABLE 6-3.—VALUES OF FOWLER'S FUNCTION $F(x)$

x	$F(x)$	x	$F(x)$
−3.0	−1.3080	8.0	1.5270
−2.5	−1.0947	10.0	1.7130
−2.0	−0.8837	12	1.8665
−1.5	−0.6741	14	1.9984
−1.0	−0.4692	16	2.1128
−0.5	−0.2676	18	2.2140
0.0	−0.0849	20	2.3046
+1.0	+0.2486	25	2.4971
2.0	0.5458	30	2.6548
3.0	0.7850	35	2.7883
4.0	0.9835	40	2.9040
5.0	1.1504	45	3.0065
6.0	1.2932	50	3.0971
7.0	1.4174		

Note: Common logarithms have been used.

It was found also that Fowler's theory could be tested and the true work function determined in a slightly different way, which offers some advantages over the one described above. Instead of plotting $F(x)$ as a function of x it was plotted as a function of $\log x$ (for $x > 0$). This yields a curve which is concave upward and approaches the horizontal for large negative values of the abscissa. At a given incident frequency ($\nu > \nu_0$), observations are then taken of the photoelectric current as a function of the temperature, and these are plotted in the form $\log I/T^2$ against $\log 1/T$. The resulting *isochromatic* curve should be of the same shape as the theoretical curve, and, after a shift parallel to itself, should be superposable on it. The vertical component of the shift is unimportant (depending on B and the units used) but the horizontal component is equal to $\log [h(\nu - \nu_0)/k]$, since from the definition of x we have,

$$\log x = \log \frac{h(\nu - \nu_0)}{k} + \log \frac{1}{T}.$$

Hence, knowing ν, the threshold ν_0 can be determined *from measurements made at a single frequency*, an interesting result. By taking measurements at other incident frequencies, other determinations of ν_0 are obtained; but it is not necessary to know the relative intensities of the spectral lines used, since reducing I to unit intensity would only introduce additional vertical shifts to the curves.

It was found that the observed curves for palladium for six different incident frequencies fitted the theoretical curve accurately, and yielded values of ϕ which agreed with each other within 1 per cent. The average value of ϕ agreed within 0.01 volt with the value 4.97 volts, obtained by analyzing data for the same specimen by Fowler's method.

For negative values of x, $F(x)$ is plotted against $\log(-x)$, and observations taken for $\nu < \nu_0$ were found to fit this curve in the same way.

CHAPTER VII

IONIZATION OF GASES AND VAPORS BY ULTRA-VIOLET LIGHT

The trend of modern physics leads us to expect a close parallelism between the effect of the impact of electrons on molecules and the effect of illuminating molecules with light whose $h\nu$ is equal to the energy of the electrons. From the point of view of straightforward and direct interpretation, perhaps the simplest type of impact is that between an electron and an atom of an alkali metal. The study of critical potentials tells us that, as the energy of the electron hitting the atom is increased step by step, successive stages of excitation can be called out, until finally, when the energy of the electron reaches a certain value, ionization takes place. We should be prepared to expect analogous results when the metallic vapor is illuminated by light of gradually increasing frequency. This expectation is fulfilled, though the parallelism is not complete. Thus, to excite the atom to the different stages, the light must have exactly the frequency of one of the lines of the principal series, whereas the electron need only have its energy equal to, or greater than, the energy change involved in the particular excitation. This kind of excitation by light is readily demonstrated by the *resonance radiation* reemitted in all directions, and by the strong absorption of the vapor for light whose frequency coincides exactly with that of its own principal series lines. To obtain evidence that ionization takes place when the frequency of the light is on the short wave-length side of the principal series limit is far more difficult, for then suitable electrodes have to be placed in the vessel containing the metallic vapor; and these electrodes, because of the condensation of the alkali metal on them, become so strongly photoelectric that, unless special precautions are taken, their surface photoelectric effects completely mask the relatively feeble ionization of the vapor. The associated continuous absorption to be expected on the short wave-length side of the principal series limit cannot be readily demonstrated because it is relatively small at low vapor pressures, while at high vapor pressures an alkali-metal vapor quickly attacks the quartz windows of the containing vessel. Nevertheless, the simplicity of the laws which may be expected to govern the ionization of alkali-metal vapors has led numerous investigators to attempt to overcome the serious experimental difficulties which have delayed the testing of the predictions of theory. It is only in the last few years that technique has been developed to the point at which we begin to have considerable confidence in the experimental results.

For reference, we tabulate the series limits of the alkali metals together with the corresponding ionization potentials. The first doublet of the principal series is also given and the associated excitation potentials.

TABLE 7-1.—CRITICAL POTENTIALS FOR THE ALKALI METALS

Elements	Series limit ($1S$)	Ionization potentials, volts	First doublet ($1S - 2P_{12}$)	Excitation potentials, volts
Li	2299A	5.368	6708A	1.840
Na	2412A	5.116	5896A 5890A	2.093 2.095
K	2856A	4.321	7699A 7665A	1.603 1.610
Rb	2968A	4.159	7948A 7800A	1.553 1.582
Cs	3184A	3.877	8944A 8521A	1.380 1.448

7-1. Vapor Pressure of the Alkali Metals.—It may also be useful to give the vapor pressures of those alkali-metal vapors for which measurements have been made. Vapor pressures can always be represented empirically by the following formula

$$\log_{10} p_{(\mathrm{mm})} = -\frac{A}{T} + B,$$

where T is the absolute temperature. Determinations of the values of the vapor pressures by different observers vary widely. The most probable values of the constants A and B, according to the "International Critical Tables," are as follows:

Element	A	B
Cs	3834	6.950
Rb	3969	6.976
K	4434	7.183
Na	5395	7.553

When only an approximate estimate of the vapor pressure is required, Table 7-2 may make the computation unnecessary.

TABLE 7-2.—VAPOR PRESSURE (MILLIMETERS)

Temperature, °C	Cs	Rb	K	Na
100	4.7×10^{-4}	2.2×10^{-4}	2.0×10^{-5}	1.2×10^{-7}
150	7.7×10^{-3}	3.9×10^{-3}	5.0×10^{-4}	6.3×10^{-6}
200	7.0×10^{-2}	3.8×10^{-2}	6.4×10^{-3}	1.4×10^{-4}
250	4.17×10^{-1}	2.43×10^{-1}	7.05×10^{-2}	1.7×10^{-3}
300	1.82	1.12	2.78×10^{-1}	1.37×10^{-2}
350	6.25	4.03	1.16	9.80×10^{-2}
400	17.9	12.0	3.93	3.44×10^{-1}
450	44.5	30.6	11.2	1.23
500	97.7	69.3	28.0	3.75
550	196.0	142.0	62.4	9.95
600	369.0	268.0	127.0	23.6

Attention is called to a recent very careful study of the vapor pressures of sodium and potassium by Edmondson and Egerton.[1] The values

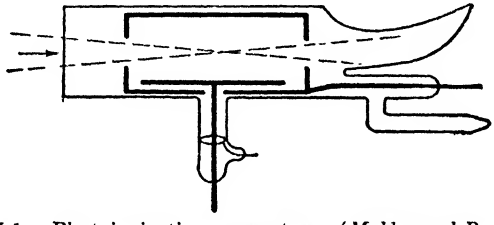

FIG. 7-1.—Photoionization apparatus. (*Mohler and Boeckner.*)

which they give for A and B are 4507.0 and 7.3447 for potassium, and 5381.3 and 7.5119 for sodium.

7-2. Photoionization of Caesium and Rubidium Vapors.—Kunz and Williams[2] concluded that Cs vapor could be ionized by ultra-violet light of wave-length shorter than 3180A. Their apparatus was similar in principle to that shown in Fig. 7-1. On heating to temperatures between 140 and 200°C, sufficient vapor pressure was obtained to show ionization by ultra-violet light from a Cooper-Hewitt mercury arc, after passing the light through a quartz monochromator. To secure sufficient intensity, bands about 80A wide had to be used.

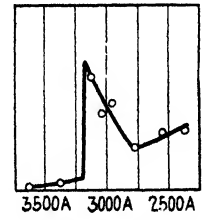

FIG. 7-2.—Photoionization in Cs. (*Little.*)

Little[3] investigated the spectral distribution of ionization in Cs vapor by means of an apparatus somewhat similar to that illustrated in Fig. 7-1. Ionization by ultra-violet light was shown by the presence of positive ions. The arrangement for securing

[1] W. EDMONDSON and A. EGERTON, *Proc. Roy. Soc.*, **113**, 539 (1926).
[2] J. KUNZ and E. H. WILLIAMS, *Phys. Rev.*, **22**, 456 (1923).
[3] E. M. LITTLE, *Phys. Rev.*, **30**, 109 (1927); **30**, 963 (1927).

monochromatic light was substantially the same as that used by Kunz and Williams. Little measured the energy passing into the caesium vapor by means of a Coblentz thermopile, and was thus able to express his results as ionization currents per unit energy, incident on the vapor. (No explicit statement was made as to whether or not his ionization currents were saturated, as of course they should have been to allow valid inferences to be made from his results.) His results are given in Fig. 7-2. It is evident that there is a strong ionization by the group of lines 3126A to 3145A on the short wave-length side of the theoretical threshold 3184A. The ionization does not completely drop to zero on the long wave-length side of 3184A. This may be due either to a small leakage of light through the monochromator along with the limited range which it is supposed to pass, or to a real ionization of a cumulative type. That the latter explanation is a possible one is proved definitely by the work of Foote, Mohler, and Chenault to be described shortly. Little tabulated and plotted his results in terms of the quantity

$$\text{(Ions formed per atom)} \div \text{(incident energy in ergs/cm}^2\text{)}.$$

This quantity is of course Einstein's coefficient B. If one assumes that ionization accounts for all the light absorbed, it is possible also to compute the *atomic absorption coefficient*, which is defined as

$$\text{(Ions formed per atom)} \div \text{(number of quanta incident/cm}^2\text{)}.$$

Mohler, Boeckner, and Coblentz[1] used the apparatus shown in Fig. 7-1 to get values of Einstein's coefficient B.

It was made of quartz and provided with a light trap at one end. One electrode is a cylinder provided with holes about 1 cm in diameter and the other is placed inside the first. Care was taken to focus the beam of light so that it did not strike either electrode. The saturation currents, which were obtained between 2 and 10 volts, were measured by a galvanometer whose sensitivity was 5×10^{-11} amp. The total energy passing through the vapor was measured by a Coblentz thermopile.

They found that the atomic absorption coefficient for Cs vapor was $(2.3 \pm 0.2) \times 10^{-19}$ at the series limit 3184A. (This is fifty times as large as the value given by Little. Because of this large difference, Mohler and Boeckner made various control experiments and concluded that the atomic coefficient could not possibly be as small as Little's value.) The atomic absorption coefficient for Rb was 1.1×10^{-19} at its series limit 2968A. Absolute values were not determined for any other metallic vapor.

Mohler, Foote, and Chenault[2] employed a most ingenious and powerful method of investigating the photoionization of Cs vapor. It depends on the phenomenon discovered by Kingdon and by Hertz, which is that

[1] F. L. Mohler, C. Boeckner, and W. W. Coblentz, *Science*, **69**, 479 (1929); see also footnote 2, p. 254.

[2] F. L. Mohler, P. D. Foote, and R. L. Chenault, *Phys. Rev.*, **27**, 37 (1926); also F. L. Mohler and P. D. Foote, *Phys. Rev.*, **26**, 195 (1925).

under certain conditions the space-charge limited currents from a hot filament may be much increased by the presence of a few positive ions. The apparatus used consists essentially of a metal cylinder C (Fig. 7-3), surrounding a loop of fine tungsten wire W which can be heated by a

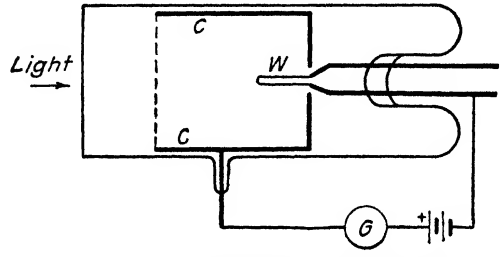

FIG. 7-3.—Space-charge method of investigating photoionization. (*Mohler, Foote, and Chenault.*)

current. The tube has nothing in it but Cs vapor whose pressure can be controlled by the temperature. When the filament is sufficiently hot, the current obtained is the space-charge limited current appropriate to the applied potential. If a single positive ion is produced within C, its low speed, as compared with the speed of the electrons in the same field, together with the fact that it may describe several loops of its orbit around W before finally falling into it, will permit the escape of 10^4 to 10^6 additional electrons. Thus the increase in the thermionic current due to the presence of a few positive ions, above its value in their absence, will be an exceedingly sensitive indicator of the presence of positive ions. The great sensitivity of the method allowed them to get measurable effects with far narrower slits in the monochromator than had been possible before. This made for greater precision in their results. Unlike any of the other methods of investigating ionization by light, this method has the great advantage that it is not necessary to guard against strong photoelectric emission from solid surfaces, for the only solid surface whose potential is favorable to the emission of photoelectrons is the filament and its area is negligibly small. (The sources of light used were a 400-watt Mazda lamp, a tungsten-filament lamp with a quartz window, and a quartz mercury arc.) Typical results are shown in Fig. 7-4. The ionization per unit energy drops away on the short wave-length side of the theoretical threshold 3184A, at first rapidly, and then more slowly and with perhaps a strong hint of a minimum at 2700A (*cf.* Little's

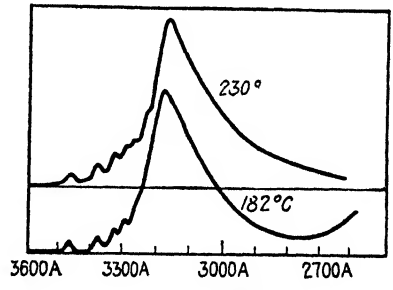

FIG. 7-4.—Spectral distribution of photoionization in Cs vapor. (*Foote, Mohler, and Chenault.*)

minimum at 2800A), at any rate for the lower temperature. The unexpected appearance of ionization by light on the long wave-length side of the threshold will be discussed in Sec. **7-7**.

The space-charge method was also used by Lawrence and Edlefsen[1] to investigate the photoionization in Cs and Rb vapors. A very powerful source of ultra-violet light was employed (see Sec. **12-19**), yielding measurable currents for highly resolved light. To secure great sensitivity they balanced the space-charge currents in two similar chambers (both

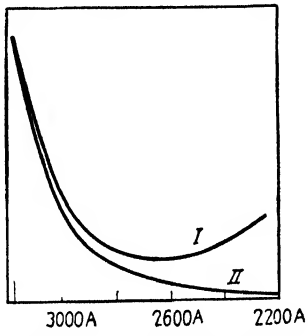

FIG. 7-5.—Photoionization in Cs vapor beyond the threshold. I. Mohler and Boeckner. II. Lawrence and Edlefsen.

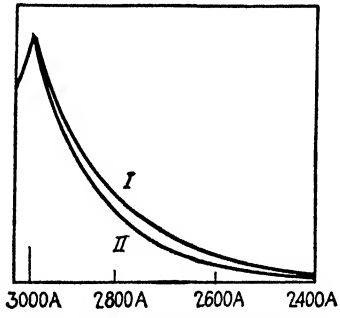

FIG. 7-6.—Photoionization in Rb vapor beyond the threshold. I. Mohler and Boeckner. II. Lawrence and Edlefsen.

in the same tube) and measured the lack of balance when one chamber was illuminated. The results are shown in Figs. 7-5 and 7-6. Mohler and Boeckner[2] investigated the ionization in Cs and Rb vapors at about the same time, also by the space-charge method. Their results are also shown in Figs. 7-5 and 7-6. It will be seen that there is satisfactory agreement as to the ionization in Rb vapor, but in the case of Cs vapor the results differ very considerably. Little and Mohler and Boeckner find a decided upturn in the ionization per unit light intensity somewhere between 2700A and 2800A, while Lawrence and Edlefsen find a continuous decrease as far as 2200A.

Mohler and Boeckner made a direct determination of the absorption coefficient of Cs vapor for 3130A and obtained the important result that, within the rather wide errors of experiment, the absorption was wholly accounted for by the ionization produced. They also found that the ionization is proportional to the pressure, that is, to the number of atoms present. This indicates that photoionization by light on the short wave-length side of the series limit consists simply in the ejection

[1] E. O. LAWRENCE and N. E. EDLEFSEN, *Phys. Rev.*, **34**, 233 (1929).

[2] F. L. MOHLER and C. BOECKNER, *U. S. Bur. Standards Jour. Research*, **3**, 303 (1929).

of an electron from the atom as a direct result of the absorption of a quantum, a process which is unaffected by the presence of other atoms.[1]

7-3. Photoionization in Potassium Vapor.—The ionization in K vapor has been investigated by two distinct methods—the space-charge method already described, and the "jet" method. The first important results were obtained by Williamson,[2] who devised the jet method. His apparatus is shown diagrammatically in Fig. 7-7.

Potassium vapor is driven upwards from a boiler containing liquid potassium at between 300 and 400°C and is condensed on a glass surface

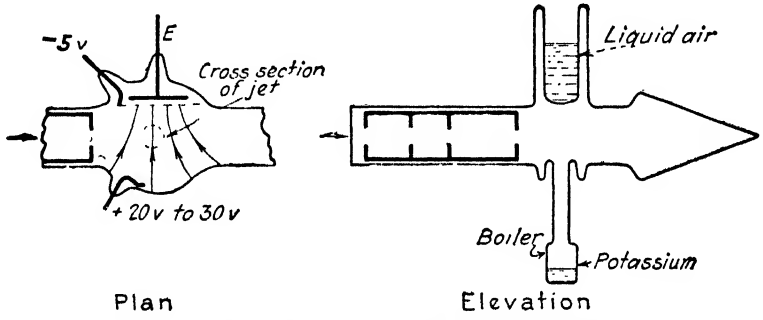

FIG. 7-7.—Jet method for investigating photoionization.

cooled by liquid air. A beam of light, carefully diaphragmed to prevent any of the light from falling on the electrodes, passes through the jet of vapor. Ionization is detected by the presence of positive ions driven from the jet to an electrode by a suitable electric field. A possible spurious photoelectric effect at the surface of E is avoided by maintaining a grid in front of it at a small negative potential to prevent the escape of photoelectrons. To determine where photoionization begins, Williamson used a number of light filters which cut off the spectrum of a quartz mercury arc at various known positions in the ultra-violet. He concluded that ionization sets in between 2800A and 3100A and, therefore, presumably at the theoretical limit for K vapor, *viz.*, 2856A. He also inferred that the efficiency of ionization increases rapidly with decreasing wave-length. Samuel's method[3] was similar in principle to that of Williamson. He concluded that ionization begins between 2804A and 2893A, which is in accord with the theoretical value 2856A.

Lawrence[4] obtained results which, for the first time, appeared to show that the photoelectric threshold of K was close to 2600A and

[1] According to a very recent investigation (F. W. COOKE, *Phys. Rev.*, **38**, 1351 [1931]), the photoionization yield in Cs vapor has a minimum at about 2800A. This result is in qualitative agreement with that of Little and that of Mohler and Boeckner and in conflict with that of Lawrence and Edlefsen.

[2] R. C. WILLIAMSON, *Phys. Rev.*, **21**, 107 (1923).

[3] R. SAMUEL, *Zeits. f. Phys.*, **29**, 209 (1924).

[4] E. O. LAWRENCE, *Phil. Mag.*, **50**, 345 (1925).

definitely not at 2856A. The apparatus resembled that sketched in Fig. 7-7, except for the fact that after traversing the jet the ultra-violet light passed through a quartz window into a photoelectric cell whose purpose was to give a sort of measure of the intensity of the light used. He found that the efficiency of ionization *increases* as one goes from the threshold to shorter wave-lengths, a result in striking disagreement with the results of Little and of Foote, Mohler, and Chenault for Cs.

Using an improved form of the jet method, Williamson[1] reexamined the photoionization of potassium and obtained a curve which indicated one threshold at about 2600A and another at about 3100A. As neither agrees with the theoretical value 2856A, Williamson attributes the threshold at 3100A to ionization of the molecule without dissociation, and the 2600A threshold to ionization with dissociation. By suitably placed grid electrodes, it was possible to investigate the energy distribution of the photoelectrons ejected from the molecules. If light of frequency ν falls upon an atom whose threshold is ν_0, it is to be expected that the electron would be ejected with energy $(h\nu - h\nu_0)$. Using incident light of two selected wave-lengths, Williamson obtained maximum emission energies which checked to about 0.2 volt with the expected values. The curves showing the number of photoelectrons emitted against various retarding potentials imply that electrons of all energies from a maximum down to zero are present. The retarding potential method does not yield an undistorted distribution of velocity curve, unless the electrodes are so disposed that the electrons approach the more negative electrode without any tangential component of velocity. Williamson's arrangement of electrodes did not satisfy this requirement, and therefore we cannot finally infer from his curves that photoelectrons ejected from gaseous molecules by monochromatic light have, as in the case of photoelectrons ejected from a solid, emission energies ranging from a maximum down to zero. The electrons emerging from a solid surface with smaller energies than the maximum are readily accounted for by loss of energy by collision on the way out. In a gas no such process is possible, provided that the electron can travel from its parent molecule to the electrode without collision. Assuming sufficiently long free paths for the electrons in the vapor, we might well expect monochromatic light to produce photoelectrons in a gas all of exactly the same energy. It would be interesting to verify this.

Further investigations have been carried out recently by Mohler and Boeckner,[2] and by Lawrence and Edlefsen,[3] on photoionization in K

[1] R. C. Williamson, *Proc. Nat. Acad. Sci.*, **14**, 793, 796 (1928).

[2] F. L. Mohler and C. Boeckner, *U. S. Bur. Standards Jour. Research*, **3**, 303 (1929).

[3] E. O. Lawrence and N. E. Edlefsen, *Phys. Rev.*, **34**, 1056 (1929).

vapor. In both cases the space-charge method was used. Lawrence and Edlefsen found *two* maxima, one at the series limit 2856A, and the other at 2340A (Fig. 7-8). The latter is about three times as high as the first. These results account in part for the earlier results with K, *viz.*, that the ionization appears to increase with diminishing wave-length. There is, however, considerable discrepancy between these results and the results of Mohler and Boeckner, who found that the photo-ionization in K increases steadily with diminishing wave-length (Fig. 7-8) without any indication of maxima or minima. The curve obtained by Lawrence and Edlefsen strongly suggests the onset of a second type of

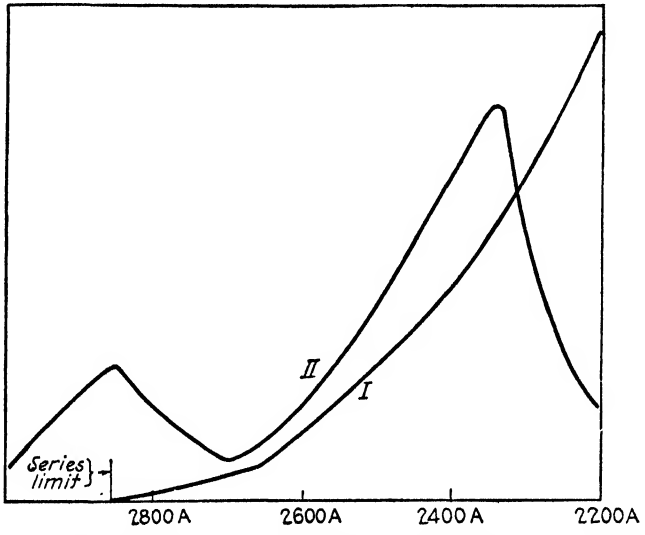

FIG. 7-8.—Photoionization in K vapor. I. Mohler and Boeckner. II. Lawrence and Edlefsen.

ionization with a threshold at a shorter wave-length than the series limit, 2856A.

This led Hughes and Van Atta[1] to look for a second ionization potential for K A discontinuity in the ionization curve plotted as a function of the energy of the electrons was interpreted as a second ionization potential, 0.97 volt above the first. Taking the first as corresponding to the series limit 2856A, the second would correspond to 2350A, which is close to the 2340A peak in Lawrence and Edlefsen's work. Although the numerical agreement is good, one would perhaps expect the onset of a second type of ionization to correspond to the foot at 2700A rather than to the peak.

7-4. Absorption of Light by Potassium Vapor.—If, beyond the principal series limit, the absorption of light is entirely accounted for by the ionization produced, then a study of the absorption of light in this region should give results in accord with those on ionization. Experiments on the absorption of light in alkali-metal vapors are difficult.

[1] A. L. HUGHES and C. M. VAN ATTA, *Phys. Rev.*, **36**, 214 (1930).

Measurable absorptions can only be obtained when considerable vapor densities are employed.[1] Under such conditions, however, the vapor readily attacks the quartz windows of the apparatus, and so it is necessary to localize the vapor in the middle part of a long iron tube by filling it with a suitable gas to a pressure of a few centimeters. Using such an apparatus, Ditchburn[2] carried out extensive measurements on the absorption of white light by potassium vapor. Typical results are shown in Fig. 7-9. If potassium atoms alone were present one would expect no absorption at all on the long wave-length side of the principal series limit, (except for the intensely strong and narrow absorption lines coinciding with the lines of the principal series), and a continuous absorption beginning at the limit and extending indefinitely. To account for his experimental curves, Ditchburn supposed that diatomic molecules of potassium were present and, in fact, were generally responsible for most of the absorption. By a method, which need not be described, Ditchburn attempted to disentangle the diatomic absorption from the atomic absorption. The dotted lines 1*a* and 2*a* indicate the shapes of the atomic absorption thus estimated. The atomic absorption diminishes from a wave-length a little on the long wave-length side of the limit 2856A to a minimum at about 2500A, and then increases. One may be tempted to associate the abrupt upward turn in the atomic absorption at about 2500A in some way with the second peak found by Lawrence and Edlefsen.

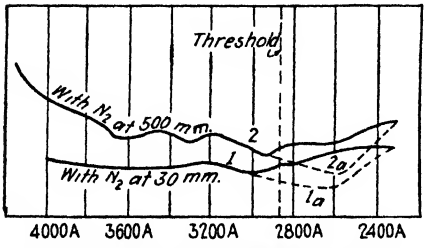

FIG. 7-9.—Absorption of light in K vapor.

7-5. Molecular Association in Alkali-metal Vapors.—The fact that ionization of potassium vapor by light does *not* begin at the limit of the principal series has been interpreted as indicating that the ionization observed is ionization of the molecule and not of the atom. It is therefore desirable to consider the evidence available for the degree of association of atoms into molecules in this vapor. This may be obtained directly from an experimental determination of the density of the alkali-metal vapor, or indirectly from a knowledge of the heats of dissociation and vaporization of the metal. The only direct experimental evidence available is that of Walter and Barratt,[3] who determined the density of potassium vapor by the Victor Meyer method at 935°C and concluded that the ratio K_2/K was probably 2 per cent and certainly less than 5 per cent. To find the fraction of molecules which are diatomic at any

[1] Recently, however, Mohler and Boeckner determined the absorption in a tube, 30 cm long, containing Cs at about 230°C ($\sim$ 0.41 mm pressure).

[2] R. W. DITCHBURN, *Proc. Roy. Soc.*, **117**, 486 (1928).

[3] J. M. WALTER and S. BARRATT, *Proc. Roy. Soc.*, **119**, 257 (1928).

pressure and temperature, we may follow Ditchburn[1] and make use of a formula developed by R. H. Fowler in his investigations in statistical mechanics. The fraction of atoms associated (γ) at any temperature (T) and pressure (p) may be found if one knows the moment of inertia of the molecule (mR^2) and the heat of dissociation (U_0).

$$\log \gamma = \log \frac{4\pi^{\frac{1}{2}} hN\, 273}{k^{\frac{1}{2}}\, 760} + \log \frac{mR^2}{m^{\frac{3}{2}}} - 1.5 \log T + \frac{U_0}{2.3kT} + \log p.$$

The first term on the right-hand side, involving Planck's constant h, the number of molecules per cubic centimeter at 273°K and 760 mm (N), and Boltzmann's constant k, is a universal constant, and equals 1.585. The second and fourth terms vary from one molecule to another. Unfortunately the values of the constants U_0 and mR^2 for the various molecules, which are of vital importance for numerical computation, vary tremendously in the few cases in which they have been determined. We have computed γ on the assumption that U_0 is 18,100 cal/gr-mol for Na_2, and 14,950 cal/gr-mol for K_2; and that mR^2 is 17.95×10^{-39} gr cm² for Na_2, and 74.0×10^{-39} gr cm² for K_2. (These values are based on information supplied to us recently by Professors Loomis and Mulliken.)

To illustrate how sensitive γ is to a change in the constants (see Table 7-3), we record (in italics) the values it takes when the most acceptable 1928 figures are used, *viz.*, 23,000 cal/gr-mol and 2.3×10^{-39} gr cm² for Na_2, and 13,000 cal/gr-mol and 18.4 gr cm² for K_2. (The mR^2 values were obtained by Smith.[2])

The pressures most frequently used in experiments are saturation vapor pressures and so it is possible to substitute for $\log p$ from the empirical linear vapor-pressure equation. The equation may then be written in this form.

$$\log \gamma = \text{const} + \log mR^2 - \log m^{\frac{3}{2}} - 1.5 \log T + \frac{U_0}{2.3kT} - \frac{A}{T} + B.$$

It is clear from this equation that the association factor γ increases with increasing temperature if the factor A involving the heat of vaporization exceeds the factor $U_0/2.3k$ involving the heat of dissociation and *vice versa*. In computing the numerical values for γ, which are given in Table 7-3, we have used the constants of Edmondson and Egerton (Sec. **7-1**). (The calculated values for potassium, given in *italics*, and therefore based on doubtful constants, are in satisfactory accord with the isolated experimental value obtained by Walter and Barratt.[3]) For unsaturated vapor maintained at constant pressure, increasing the temperature diminishes γ. This corresponds to the case where a side

[1] R. W. Ditchburn, *Proc. Roy. Soc.*, **117**, 486 (1928).
[2] H. G. Smith, *Proc. Roy. Soc.*, **106**, 400 (1926).
[3] J. M. Walter and S. Barratt, *Proc. Roy. Soc.*, **119**, 257 (1928).

TABLE 7-3.—MOLECULAR ASSOCIATION IN ALKALI-METAL VAPORS

Temperature		γ(Na)		γ(K)	
177°C	450°K	0.0069	*0.371*	0.022	*0.00038*
277°C	550°K	0.017	*0.213*	0.046	*0.00132*
377°C	650°K	0.035	*0.140*	0.076	*0.00300*
477°C	750°K	0.053	*0.098*	0.110	*0.00529*
577°C	850°K	0.076	*0.075*	0.130	*0.00797*
677°C	950°K	0.096	*0.059*	0.160	*0.01080*

tube of the apparatus is kept at a fixed temperature lower than the temperature of the apparatus and the latter temperature is varied.

No data are available by which we may compute γ for caesium.

7-6. Concerning the Nature of Photoionization.—We shall discuss in this section the photoionization produced by light of wave-length shorter than that of the series limit. (The ionization observed with light on the long wave-length side of the limit, due to line absorption, is discussed in the next section.) It is natural to assume that it is the atom which is ionized when the threshold is where it should be, *viz.*, at the series limit. This is the case for Cs and Rb, but at first it appeared not to be the case for K. The recent work of Lawrence and Edlefsen, however, has also revealed a threshold in K at the series limit, so that, apart from the presence of the second maximum in its curve, K, Rb, and Cs are all similar. In the absence of evidence to the contrary, we may assume the absorption to be accounted for entirely by photoionization, so that theories giving the absorption at various wave-lengths, on the short wave-length side of the series limit, can be tested by the photoionization curves. Theories have been given by Kramers[1] and by Milne,[2] predicting that the photoionization should vary as λ^4 and λ^3, respectively. The experimental curves (Figs. 7-5 and 7-6) fall off much more steeply than either of these two predictions.

Richardson[3] has pointed out how a theory which he developed primarily for computing the photoelectric emission from solid surfaces is also applicable to photoionization. (Since the argument is thermodynamical, there is no restriction as to mechanism.) A summary of the theory is given in Sec. **6-10.** It will be seen there that he equates

$$N_1 = AT^2e^{-\frac{h\nu_0}{kT}},$$

the number of electrons striking unit area of a surface, per unit time, to the number of electrons leaving it, *viz.*,

[1] H. A. KRAMERS, *Phil. Mag.*, **46**, 836 (1923).
[2] E. A. MILNE, *Phil. Mag.*, **47**, 209 (1924).
[3] O. W. RICHARDSON, *Phil. Mag.*, **47**, 975 (1924).

$$N_2 = \frac{c}{4}\int F(\nu)E(\nu, T)d\nu.$$

Let us now express this in terms of collisions (leading to recombination) between electrons and ions (which is the reverse process to ionization). If the collision area of the ion is q, then the number of electrons hitting the ion, in unit time, is

$$N_1' = N_1 q.$$

On the other side the number of times the atom is ionized, per unit time, is equal to

$$N_2 = \frac{c}{4}\int B_\nu E(\nu, T)d\nu,$$

where B_ν is the probability of absorption of a quantum in isotropic radiation of unit intensity. Then, equating N_1' and N_2, and carrying the argument through exactly as in Sec. **6-10**, we obtain

$$\frac{B_\nu}{q} = \frac{\nu - \nu_0}{\nu^3} \times \text{const.}$$

Various expressions for q, the effective collision area between an ion and an electron, may be considered. One, due to J. J. Thomson, is that it is inversely proportional to the fourth power of the relative velocity v, which, since

$$\tfrac{1}{2}mv^2 = h\nu - h\nu_0,$$

gives

$$q \propto \frac{1}{(\nu - \nu_0)^2}.$$

We then get

$$B_\nu = \frac{1}{(\nu - \nu_0)\nu^3} \times \text{const},$$

an expression which agrees fairly satisfactorily with the curves for Rb and Cs, provided that we ignore the range within 100A of the threshold, because at the threshold the expression becomes infinite. (It does not, of course, apply to those experimental curves for Cs which show an upturn at about 2500A.)

Because the photoionization curves for K are so different from those for Cs and Rb, in which the effect is presumably due only to the atom, it has been thought necessary to attribute part of the photoionization in K to the molecule. There are, however, weighty objections to this view.

1. The data given in Table 7-3 indicate that, under the experimental conditions usually obtaining, there is roughly but one molecule for every 100 atoms. We should therefore expect the molecule to be responsible for a negligible fraction of the ionization unless the absorption of the

molecule is enormously larger than that of the atom, a view difficult to justify.

2. Ditchburn and Arnot[1] measured the e/m for the ions produced in K vapor by ultra-violet light. They found K^+ ions only, they did not find any K_2^+ ions. (Although the natural interpretation of this is that the atom is ionized by the light, the authors, however, interpreted their results as indicating the production of a K_2^+ ion from a K_2 molecule, the K_2^+ ion dissociating immediately into K^+ and K.)

3. Ditchburn's curve (Fig. 7-9) indicates a pronounced upturn in the *atomic* absorption coefficient at about the same place that the rise to the second peak starts. It appears that the weight of evidence at present is in favor of regarding the second peak in the photoionization curve for K as of atomic origin, though no explanation can be given as to why it occurs.

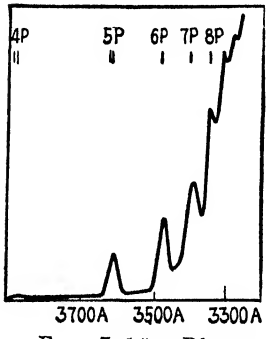

FIG. 7-10.—Photoionization on the long wave-length side of the threshold. (*Foote, Mohler, and Chenault.*)

7-7. Photoionization by Lines of the Principal Series.—According to Mohler, Foote, and Chenault,[2] photoionization in Cs vapor is produced not only by light of wave-length shorter than the series limit, but also by light of longer wave-length. The dependence on wave-length is shown in Fig. 7-4 and, in finer detail, in Fig. 7-10. It is clear that photoionization is the result of absorption of monochromatic light whose wave-length coincides with that of one or other of the lines of the principal series. Experiment shows that the coincidence has to be exact.[3] Mohler, Foote, and Chenault found photoionization with the fourth, fifth, . . . and tenth lines of the principal series. (Beyond the tenth line, the resolution of the monochromator was insufficient to permit the separation of the effects due to individual lines.) Lawrence and Edlefsen[4] record photoionization in Rb vapor by the fourth, fifth, and sixth lines. Later, Mohler and Boeckner[5] found a small effect in Cs vapor when illuminated by the third line. Very recently Freudenberg[6] discovered that, given sufficient illumination, *all* the lines of the principal series produce photoionization in Cs vapor.

In the study of this type of photoionization, the space-charge method described in Sec. **7-2** has been used by all investigators. Unfortunately,

[1] R. W. DITCHBURN and F. L. ARNOT, *Proc. Roy. Soc.*, **123**, 516 (1929).

[2] F. L. MOHLER, P. D. FOOTE, and R. L. CHENAULT, *Phys. Rev.*, **27**, 37 (1926).

[3] The apparent finite width of the band of active light at each line is due merely to the limited resolving power of the monochromator used.

[4] E. O. LAWRENCE and N. E. EDLEFSEN, *Phys. Rev.*, **34**, 233 (1929).

[5] F. L. MOHLER and C. BOECKNER, *U. S. Bur. Standards Jour. Research*, **5**, 51 (1930).

[6] K. FREUDENBERG, *Zeits. f. Phys.*, **67**, 417 (1931).

when the pressure and temperature are varied in order to unravel the nature of the ionization, the ratio between the number of ions produced and their effect on the space-charge current changes in a complicated manner. It is therefore always necessary to measure what is called the "relative sensitivity." The relative sensitivity for 3612A, for example, is defined as the ratio:

$$\frac{\textit{Change in space-charge current due to } 3612A \textit{ per unit intensity}}{\textit{Change in space-charge current due to } 3130A \textit{ per unit intensity}}.$$

The 3130A in the denominator may be replaced by any other convenient standard, so long as it is on the *short wave-length* side of the threshold. The ionization due to 3130A (or its substitute) is a simple process, the ejection of an electron from an atom as the immediate result of the absorption of a quantum; this is the reason for using it as a standard of reference. The "quantum efficiency," *i.e.*, the probability of ionization ultimately following the absorption of a quantum of, for example, 3612A, is obtained by multiplying its relative sensitivity by the ratio of the absorption coefficient for 3612A to that for 3130A. This assumes that the quantum efficiency for 3130A (or for any radiation on the short wave-length side of the limit) is unity. This appears to be the case (Sec. **7-2**).

The direct result of the absorption of a quantum corresponding to any line in the principal series is excitation of the atom. There is not enough energy to produce ionization; yet ionization is observed. It is therefore necessary to find out what additional process brings this about. The following explanations have been suggested:

1. The extra energy required is supplied by the kinetic energy disappearing when an excited atom collides with a neutral atom.
2. The electrons constituting the space-charge current have sufficient energy ($\sim$1 volt) to ionize the excited atoms.
3. Two excited atoms collide; one takes all the energy which is sufficient to ionize it.
4. An excited atom absorbs the necessary amount of energy to complete the ionization from the infra-red radiation from the filament or from the illuminating agent.
5. The collision of an excited atom and a neutral atom results in an ionized *molecule*, whose ionization potential is lower than that of an atom (Franck's view).

Experiments on the dependence of the photoionization on the intensity of the light, the pressure, the electron current, and the temperature, together with considerations as to the probability of occurrence of some of the processes suggested, rule out all but 5. Some of the information obtained by Mohler and Boeckner and by Freudenberg as to the characteristics of the photoionization in Cs vapor by the various lines is summarized in Table 7-4. For all lines (except the first), the photo-

ionization is directly proportional to the intensity of the light; hence photoionization cannot result from the collision of *two* excited atoms. Except for the second line, the photoionization is independent of the temperature. Hence no part of the energy can come from the kinetic energy of the colliding atoms, for otherwise the ionization would increase because of their greater kinetic energy at higher temperatures.

According to Franck's view, an excited Cs atom (designated as Cs*) collides with a neutral atom, forming an ionized molecule, the process being represented by the equation,[1,2]

$$Cs^* + Cs = Cs_2^+ + e. \tag{7-1}$$

When a collision of this sort occurs, the energy of excitation supplies part of the energy necessary for ionization.

TABLE 7-4.—CHARACTERISTICS OF PHOTOIONIZATION BY LINES OF THE PRINCIPAL SERIES

Lines					Dependence on		
Number	Wavelength	Symbol	Volt equivalent	Defect from ionization potential, volts	Light intensity, K	Temperature, T	Pressure, p
1	8521A	$1S$-$2P$	1.45	2.43	$\propto K^2$	No. inf.	No inf.
2	4555A	$3P$	2.72	1.16	$\propto K$	Increases with T	No inf.
3	3876A	$4P$	3.19	0.69	$\propto K$	Independent of T	Increases with p
4	3612A	$5P$	3.42	0.46	$\propto K$	Independent of T	Increases with p
5	3477A	$6P$	3.56	0.32	$\propto K$	Independent of T	Increases with p
6	3398A	$7P$	3.64	0.24	$\propto K$	Independent of T	Increases with p
7	3347A	$8P$	3.70	0.18	$\propto K$	Independent of T	Increases with p
8	3313A	$9P$	3.73	0.15			
9	3289A	$10P$	3.75	0.13			
10	3270A	$11P$	3.78	0.10			

No inf. = no information.

If a collision does not occur within the "life" of the excited atom, its energy disappears as radiation and no ion is formed. It is evident, therefore, that the amount of photoionization should increase with the pressure until such a pressure is attained that no excited atom has a chance to radiate before collision. Mohler and Boeckner studied the pressure effect in detail. Starting with the formula,

$$P = \frac{\mathfrak{I}}{T + \mathfrak{I}},$$

where P is the probability of collision within the life of the excited atom, $\mathfrak{I}$ the average life, and T the average time between collisions, they deduced that

[1] This view is attributed to J. Franck in B. Gudden's "Lichtelektrische Erscheinungen," p. 226 (Julius Springer, 1928).

[2] Cs* refers to any excited state: it is convenient to use Cs′, Cs″, . . . to refer to the particular excited states $2P$, $3P$, . . .

$$\frac{1}{E} = \frac{1}{E_0}\left(1 + \frac{1}{A\sigma^2 \mathfrak{I} p}\right)$$

where E is the quantum efficiency, σ the distance between atomic centers at collision, p the pressure, and the other quantities are constants. Thus $1/E$ should be a linear function of $1/p$; this was found to be the case experimentally. The maximum quantum efficiencies for each wavelength, *i.e.*, E_0 (the value of E in the above equation when p is sufficiently large to make the last term negligible) increase from 0.0067 at 3887A and 0.19 at 3619A to very nearly unity for lines close to the limit. A tentative explanation offered by Mohler and Boeckner is given in the last paragraph of this section. Experiments on photoionization in the pres-

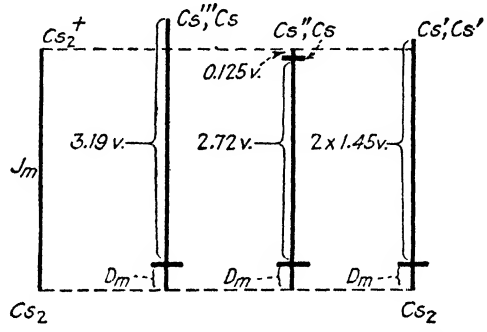

FIG. 7-11.—Energy relations in photoionization.
J_m = ionization potential of Cs_2;
D_m = heat of dissociation of Cs_2:
Cs', Cs'', Cs''', excited atoms in the $2P$, $3P$ and $4P$ states.

ence of various gases gave additional evidence as to the effect of various kinds of collisions.[1]

According to Table 7-4, the ionization due to the first and second lines differs in certain respects from that due to the rest. We note that for the second line the photoionization increases with the temperature, while for the third, fourth, . . . lines it is independent of the temperature. In the latter case, the energy of the excited atom plus the heat of dissociation of the molecule are more than sufficient to ionize a molecule. For the second line (4555A), however, ionization results only when enough *additional* energy can be acquired from the kinetic energy involved in a collision. Hence, since raising the temperature increases the average kinetic energy, it is easy to see why the photoionization in this special case increases with the temperature. From the rate of increase Freudenberg estimated that the extra energy required over and above that supplied by the excited atom ($3P$ state) is 0.125 ± 0.025 volt. These

[1] F. L. MOHLER and C. BOECKNER, *U. S. Bur. Standards Jour. Research*, **5**, 399 (1930).

considerations are represented diagrammatically in Fig. 7-11. (As might be expected, the quantum efficiency of 4555A is extremely low.)

To obtain photoionization by the first line (8521A), intense illumination is required. The fact that the photoionization increases as the *square* of the light intensity indicates that the ionized molecule results from a collision between *two* excited atoms, or

$$Cs' + Cs' = Cs_2^+ + e.$$

In the absence of a direct test of the effect of change of temperature on the yield, it may be presumed that the excitation energy (2 × 1.45 volts) together with the heat of dissociation is sufficient to produce an ionized molecule (Fig. 7-11).

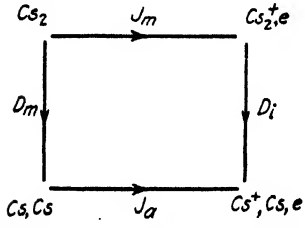

FIG. 7-12.—Energy diagram for Cs_2.

Freudenberg correlates the ionization potentials of the Cs_2 molecule and of the Cs atom, with the heats of dissociation of the neutral and the ionized molecule, from his experimental data, in the following manner. A consideration of the energy diagram (Fig. 7-12) shows that

$$J_m + D_i = J_a + D_m, \tag{7-2}$$

where

J_m = ionization potential of the molecule.
J_a = ionization potential of the atom.
D_m = heat of dissociation (in volts) of the neutral molecule.
D_i = heat of dissociation of the ionized molecule in volts.

On writing Cs″ for Cs* (since we are dealing with the $3P$ excited state), we get from Eq. (7-1) and the data shown in Fig. 7-11:

$$Cs'' + Cs + 0.125 \text{ volt} = Cs_2^+ + e$$

or, since, approximately,

$$Cs'' = Cs + 2.7 \text{ volts}$$

and

$$Cs_2^+ = Cs + Cs + J_m - D_m$$

(Fig. 7-12), we have

$$2.7 \text{ volts} + 0.12 \text{ volt} = 2.82 \text{ volts} = J_m - D_m. \tag{7-3}$$

Equation (7-2) gives

$$J_m - D_m = J_a - D_i,$$

and since we know J_a, the ionization potential of the Cs atom, to be 3.88 volts, we find that the *heat of dissociation of the ionized molecule* is

$$D_i = 1.06 \text{ volts.}$$

The heat of dissociation of the neutral molecule is not known, but band spectra give values for Li_2, Na_2, and K_2, from which it may be estimated by extrapolation that D_m for Cs_2 is about 0.35 volt. On inserting this in Eq. (7-3) we find that the *ionization potential of the molecule* is

$$J_m = 3.17 \text{ volts.}$$

With these numerical results we can proceed to draw Franck-Condon diagrams for various molecules (Fig. 7-13). A point on the extreme right

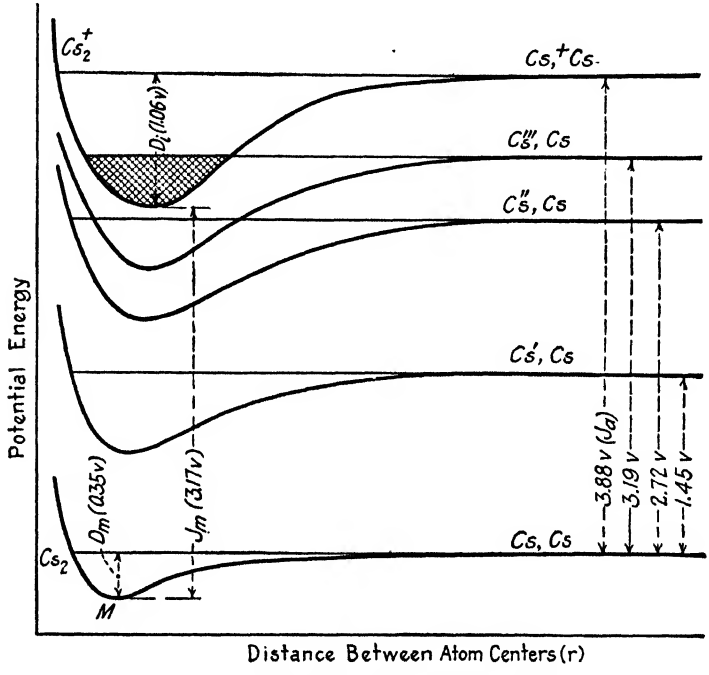

FIG. 7-13.—Franck-Condon diagram for Cs.

of the lowest curve represents a dissociated molecule, *i.e.*, one with its two atoms widely separated. The point M represents the molecule when the atoms are at such a distance apart that the potential energy is a minimum; this is the normal state of the molecule. In the same way, the uppermost curve refers to an ionized molecule, the extreme right corresponding to the ionized molecule dissociated into a neutral atom and an ionized atom. The other curves refer to various kinds of excited molecules. It is evident that the vertical spacing of the curves at the extreme right is given by the excitation and ionization energies of the *atom*. The depths of the "valleys" represent the energy necessary to dissociate the various molecules. The collision of an excited atom and a neutral atom (say, Cs''' with Cs) is represented by a point on the curve moving from

the extreme right of the corresponding curve towards the left and then oscillating to and fro across the valley. The kinetic energy may be emitted in quanta (associated with the band spectrum), leaving the excited molecule with the minimum amount of potential energy; *i.e.*, it no longer vibrates and its state corresponds to the bottom of the valley. But if the horizontal line, to which the curve approaches as $r \rightarrow \infty$, representing the mutual energy of the excited atom and the neutral atom, is *above* the lowest part of the valley for the *ionized* molecule Cs_2^+, it is possible for the latter to be formed. Thus the collision of Cs''' with Cs may result in Cs_2^+, but unless extra energy is forthcoming from some other source, we cannot get Cs_2^+ from a collision between Cs'' and Cs. Further, Mohler and Boeckner have suggested that the probability of the formation of a Cs_2^+ molecule from one excited atom and one neutral atom depends on the area intercepted between the valley for Cs_2^+ and the horizontal line measuring the energy of the two atoms when far apart. Thus, for the Cs''' atom the area referred to is heavily shaded. For atoms in a higher state of excitation the intercepted area will be larger. Hence we can account for the increase in the yield of ions as we go from Cs''' to Cs atoms in higher states of excitation.

7-8. Ionization of Caesium Vapor by Absorption between the Series Lines.—According to Fig. 7-10, some ionization is produced by light whose wave-length is between that of the lines of the principal series. This might be attributed to imperfect action on the part of the monochromator, but Boeckner and Mohler[1] have shown that it is a real effect. The *relative sensitivity*, as defined in the previous section, increases from 0.0003 at 3750A to 0.07 at 3250A. It increases roughly as the square root of the pressure at all wave-lengths. It decreases with increasing temperature so long as the light is of shorter wave-length than 3500A, while if the light is of longer wave-length, it is practically independent of the temperature. Is it a molecule, or is it an atom, which is involved in this effect? If it be allowed that each line of the principal series, ordinarily considered to be extremely narrow, really extends indefinitely on both sides (though in very attenuated form), one can assume that the atoms absorb light to a very small extent between the centers of the lines and can therefore be ionized. Boeckner and Mohler calculate that the relative sensitivity should in this case be proportional to the square root of the pressure, as was found by experiment. The effect of temperature is in conflict with this view. The relative sensitivity for ionization by the lines is independent of the temperature for lines of wave-length shorter than 4555A for here the *atom* absorbs the line radiation; and although we eventually get a molecular ion, a change in the atom is the first effect. Boeckner and Mohler then consider the possibility of the

[1] C. Boeckner and F. L. Mohler, *U. S. Bur. Standards Jour. Research*, **5**, 831 (1930).

molecules being the absorbers of the light, even though the atoms far outnumber them. The proportion of molecules to atoms may be expected to decrease with increasing temperatures, and so it is possible qualitatively to account at least for the effect between 3500A and the series limit. (According to Fig. 7-13, the minimum ionization potential of the Cs_2 molecule is 3.17 volts, which would imply a threshold of about 3900A. It is probably impossible to test this because of the extremely small effects. However, measurable effects were obtained at 3800A.) Boeckner and Mohler believe that if they are dealing with the molecule their results are in accord with the view that absorption of light *first* changes the normal molecule into a highly excited molecule, which *then* spontaneously passes over into a molecular ion if it has energy enough. It is worthy of note that, although the absorption between the lines is extremely small compared with that of the absorption of the lines, the ionization itself is an appreciable fraction of that at the limit.

7-9. Ionization in Mercury Vapor by 2536A.—It is now well established that, in order to ionize a mercury atom by collision with an electron, the electron must have a minimum energy of 10.4 volts. This is in excellent accord with the value of the series limit of mercury, 1188A (10.39 volts). Consequently we should expect ionization by light to begin at 1188A.

Steubing[1] found that the light from a quartz-mercury lamp caused a small current to pass between two electrodes in a quartz tube containing mercury vapor. He believed that the effect was a real ionization of the vapor and could not be attributed to a photoelectric effect at the surface of the electrodes. Since the light from a quartz-mercury lamp does not contain radiation of wave-length shorter than 1849A, this result is in sharp disagreement with the predictions of theory. In the light of experiments, shortly to be described, it is probable that the precautions taken to eliminate a photoelectric effect at the surface of the electrodes were not adequate.

An interesting type of cumulative ionization of mercury vapor by light was discovered by Rouse and Giddings.[2] The vapor was contained in a quartz tube containing two parallel electrodes whose areas were roughly as 6 to 1. When light from an ordinary hot mercury lamp was directed into it, the measured currents changed approximately in the same ratio when the direction of the field between the electrodes was reversed. This clearly indicates that the observed current is due to a photoelectric effect at the electrodes arising from scattered ultraviolet light. (Direct illumination was avoided by shielding.) When, however, a water-cooled mercury lamp was used, in which there is no reversal of

[1] W. Steubing, *Phys. Zeits.* **10**, 787 (1909).

[2] G. F. Rouse and G. W. Giddings, *Proc. Nat. Acad. Sci.*, **11**, 514 (1925); **12**, 447 (1926).

the center of the line 2536A, it was found that the current was larger the higher the pressure of the mercury vapor and, moreover, that the magnitude of the current became independent of the direction of the field at an appreciable pressure. This points strongly to a real ionization of the gas. The energy of a quantum of 2536A radiation is equivalent to only 4.9 volts, whereas energy corresponding to 10.4 volts is needed for ionization. Consequently some sort of cumulative action probably takes place. An atom, excited to the 2^3P_1 state (4.9 volts), requires $10.4 - 4.9 = 5.5$ volts energy to complete the ionization. This could be supplied by light of any wave-length shorter than 2340A. Direct experiment, however, showed that the effect was the same whether such radiation was present or not. Further tests showed that the effect was due entirely to the "core" of the line 2536A. It should be noted that either the absorption of two 2536A quanta by the same atom (if that were possible), or the collision of two atoms, both in the 2^3P_1 state (leading to a transfer of all the excitation energy to one of them), would still leave $10.4 - (2 \times 4.9) = 0.6$ volt to be acquired somehow. That the effect is a two-stage cumulative process is strongly supported by the fact that the ionization current is proportional to the *square* of the intensity of the active radiation. (In their second paper, Rouse and Giddings find the current to become more nearly proportional to the *cube* of the intensity as the pressure of the mercury vapor is raised considerably further, *i.e.*, to about 30 mm.)

Much light has been thrown on the details of the cumulative ionization in mercury vapor by the work of Houtermans.[1] He made skillful use of the results of Stuart,[2] Meyer,[3] and others[4] on the effect of the addition of foreign gases on resonance radiation from this vapor. According to these results, the absorption of resonance radiation puts the mercury atom into the excited 2^3P_1 state, which lasts only about 10^{-7} sec, after which the atom returns to the normal state, emitting a quantum of 2536A radiation. The intensity of the reemitted radiation is a measure of the number of atoms which can terminate their excited state by the radiation of 2536A before collision with another atom interferes. The addition of certain gases, such as hydrogen and oxygen, greatly reduces the intensity of resonance radiation; this effect increases very rapidly with the pressure of the added gas. A collision of an excited mercury atom in the 2^3P_1 state with a hydrogen molecule results in the dissociation of the molecule, thus using up the energy which otherwise would have gone into radiation.

[1] F. G. Houtermans, *Zeits. f. Phys.*, **41**, 619 (1927).

[2] H. A. Stuart, *Zeits. f. Phys.*, **32**, 262 (1925).

[3] E. Meyer, *Zeits. f. Phys.*, **37**, 639 (1926).

[4] P. Pringsheim, "Fluorescenz und Phosphorescenz," p. 125 (Julius Springer, 1928); J. Franck and P. Jordan, "Anregung von Quantensprüngen durch Stösse," p. 225 (Julius Springer, 1926).

The addition of certain other gases, such as helium, neon, argon, and nitrogen, has relatively very little effect on the intensity of the resonance radiation. In many of the collisions between molecules of these gases and excited mercury atoms, the latter are transformed from the excited 2^3P_1 state (4.9 volts) into the metastable 2^3P_0 state (4.7 volts). This metastable state has an extremely long life (10^{-2} sec).[1] Meyer found that the rate of dissociation of a small amount of hydrogen in the presence of mercury vapor, illuminated by resonance radiation, was increased by the presence of an appreciable quantity of nitrogen. The explanation is that the nitrogen molecules convert many of the short-lived excited mercury atoms (the 2^3P_1 state) into the long-lived metastable atoms (the 2^3P_0 state), and so there is a greater opportunity for a hydrogen molecule to be dissociated by either excited or metastable mercury atoms than by excited atoms alone. Houtermans used an experimental arrangement very similar in principle to that of Rouse and Giddings. His electrodes were of molybdenum which was insensitive photoelectrically to 2536A. By a variety of tests, he showed that the "core" of 2536A, and that alone, was responsible for the observed ionization. The ionization current was found to be proportional to the square of the intensity of the radiation within the range of pressures used (0.002 to 5 mm). Since there is not enough energy in a quantum of 2536A radiation to ionize a mercury atom, one must postulate a two- or three-stage process. A two-stage process is to be inferred from the fact that the ionization current is proportional to the square of the intensity of the light. Two difficulties are immediately obvious. In the first place, two quanta of 2536A radiation are insufficient for ionization of a mercury atom by 0.6 volt. In the second place, the life of an excited atom is so short ($\sim 10^{-7}$ sec) that it would, in almost every case, lose its energy by radiation before acquiring the second quantum, either directly or by collision with a second excited atom. Houtermans' view is that some of the excited mercury atoms on collision with normal atoms pass into the long-lived metastable 2^3P_0 state. A 2^3P_0 atom (4.7 volts) may collide with another 2^3P_0 atom, resulting in one atom possessing 9.4 volts energy; or else a 2^3P_0 atom may collide with an excited 2^3P_1 atom (4.9 volts), resulting in one of them acquiring 9.6 volts energy. That the latter process is the one which occurs is supported by the following considerations. In Fig. 7-14 we have a curve showing the way in which the ionization falls off with the amount of added hydrogen. With the mercury at 65°C, hydrogen at 0.026 mm reduces the ionization to one-half, while, when the mercury was raised to 150°C, hydrogen at 0.01 mm sufficed to reduce the ionization to one-half. In the same diagram are shown the results of Stuart on the quenching of resonance radiation by the addition

[1] H. B. Dorgelo, *Zeits. f. Phys.*, **34**, 766 (1925).

of hydrogen. To reduce the intensity of resonance radiation to one-half at room temperature requires 0.2 mm of hydrogen, and, it may be calculated, that 0.08 mm of hydrogen will therefore halve the number of collisions of 2^3P_1 atoms with each other. Since the ionization is reduced to one-half by a far smaller amount of hydrogen, it is evident that one at least of the colliding mercury atoms must possess a longer life than that of the 2^3P_1 atom. That this is the case is shown in the experiments in which argon is added. With mercury at room temperature, Houtermans found that the ionization current increased linearly to a value seventeen times as large as the original value, as the pressure of the argon was changed from 0 to 60 mm. It is natural to assume that, under the conditions of the experiment, the number of excited 2^3P_1 atoms converted

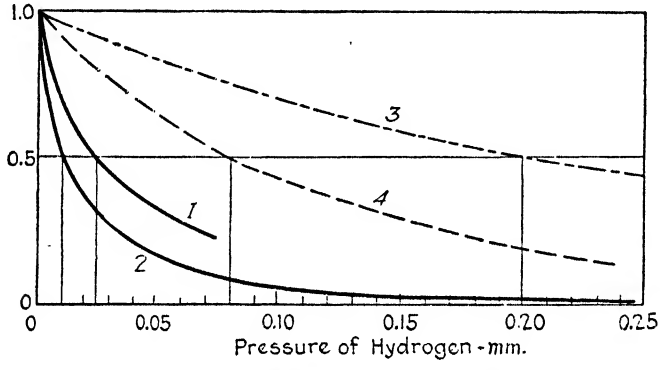

FIG. 7-14.—Photoionization in Hg-H_2 mixtures. 1. Photoionization at 65°C. 2. Photoionization at 150°C. 3 Number of 2^3P_1 atoms present at room temperature. 4. Number of collisions between 2^3P_1 atoms at room temperature (3 and 4 are calculated from Stuart's data).

into the metastable 2^3P_0 atoms increased in proportion to the amount of argon present. Hence the fact that the ionization current increased linearly with the argon pressure led Houtermans to infer that ionization takes place as a result of a collision between a 2^3P_0 atom and a 2^3P_1 atom. If a collision of two 2^3P_0 atoms with one another led to ionization, one would expect the ionization current to increase as the square of the amount of added argon, for this would presumably be proportional to the square of the number of 2^3P_0 atoms. Since the ionization is proportional only to the square of the intensity of the radiation, each ionization must depend on only two absorptions. The evidence just reviewed indicates that the ionization is a result of the collision of two mercury atoms, each of which has absorbed a quantum of 2536A radiation, one being in the excited state and the other having been converted into the metastable state. The energy accumulated in this process is 4.9 + 4.7 = 9.6 volts, which is 0.8 volt short of the amount necessary for ionization. Houtermans therefore suggests that the positive ion is a molecular ion, Hg_2^+. The results just given indicate that

$$Hg(2^3P_0) + Hg(2^3P_1) = Hg_2^+ + e$$

or

$$Hg + 4.7 \text{ volts} + Hg + 4.9 \text{ volts} = Hg_2^+ + e.$$

On the other hand, the collision of two 2^3P_0 atoms does *not* lead to an ionized molecule, so that

$$Hg + 4.7 \text{ volts} + Hg + 4.7 \text{ volts} \neq Hg_2^+ + e.$$

Hence, we may infer that two neutral atoms, plus more than 9.4 but less than 9.6 volts, cannot combine to form a molecular ion of Hg. Therefore, using the notation developed in Sec. **7-7** for Cs, we have, with obvious changes,

$$Hg + Hg + 9.5 \text{ volts} = Hg_2^+ + e = Hg + Hg + J_m - D_m$$

yielding

$$J_m - D_m = 9.5 \text{ volts}.$$

This means that the ionization potential of the neutral molecule of Hg is equal to 9.5 volts, plus the unknown heat of dissociation of the neutral molecule.[1] Applying Eq. (7-2), we find that the heat of dissociation of the ionized molecule should be

$$D_i = 10.4 - 9.5 = 0.9 \text{ volt}.$$

It would be interesting to test the truth of these views as to the nature of the ion by a direct determination of its e/m.

Foote[2] applied the space-charge method, used with such success in the investigations on the ionization of caesium vapor, to a study of the ionization of mercury vapor by resonance radiation. He found that this ionization was proportional to $I^2/(1 + BI^2)$, where I is the intensity of the radiation. This holds over a temperature range from 20 to 60°C. When the intensity is small the effect becomes proportional to I^2, as found by Houtermans. The effect was greatly increased by the addition of N_2 (which facilitates the transformation of 2^3P_1 atoms into 2^3P_0 atoms), while small amounts of hydrogen diminished the effect strongly. Hydrogen at 0.0002 mm reduced the ionization current to half value. This was presumably in the presence of nitrogen, for otherwise the results do not agree with Houtermans' values of 0.01 to 0.026 mm for the pressure of hydrogen necessary to reduce the ionization to half value.

7-10. Ionization in Air by Ultra-violet Light.—Although experiments on the photoionization of air and other permanent gases have been carried out intermittently ever since the photoelectric effect was first discovered,

[1] After the manuscript had gone to press, J. G. Winans (*Phys. Rev.*, **37**, 897 [1931]) published a value of 0.15 volt for D_m, the energy of dissociation of the neutral molecule of mercury.

[2] P. D. Foote, *Phys. Rev.*, **29**, 609 (1927).

it must be admitted that the state of our knowledge regarding the ionization of these gases is extremely unsatisfactory. Much more progress has been made in the study of ionization of metallic vapors by light, if we measure progress by our ability to interpret the results and to correlate them with the accepted systems of energy levels within the atoms. The quantum theory leads us to expect that the energy necessary to ionize a molecule should be the same whether the energy is supplied in the form of the kinetic energy of an electron or in a quantum of radiation. Consequently, the threshold of ionization by light should correspond exactly to the ionizing potential. It is the absence of this correlation which makes the photoionization observed in air difficult to interpret. The ionizing potentials of many permanent gases were determined by Mackay[1] and Morris.[2] The values are given in Table 7-5 together with the equivalent thresholds.

TABLE 7-5.—THRESHOLDS CORRESPONDING TO IONIZATION POTENTIALS

Gas	Ionization potential, volts	Threshold	Gas	Ionization potential, volts	Threshold
O_2	12.5	990A	Cl_2	13.2	940A
N_2	16.3	760A	Br_2	12.8	970A
H_2	15.8	780A	I_2	10.0	1230A
CO	14.1	880A	HCl	13.8	890A
CO_2	14.3	860A	HBr	13.2	940A
NO	9.5	1300A	HI	12.8	970A
CH_4	14.4	860A	NH_3	11.1	1110A
C_2H_6	12.8	970A	H_2S	10.4	1190A
C_2H_4	12.2	1010A	H_2O	13.2	940A
C_2H_2	12.3	1000A			

With the solitary exception of NO, it will be seen that the ionization potentials are all higher than 10.0 volts, and consequently we should expect the wave-length of the photoionization thresholds to be shorter than 1234A. In particular, we should expect the threshold for air to be farther in the ultra-violet than 990A, and yet the experiments to be described indicate that the threshold wave-length is approximately 1350A. Investigations of photoionization by light of wave-length shorter than about 1250A are badly handicapped by the fact that it is impossible to find a material to serve as a window between the source of radiation and the gas whose ionization is being investigated. According to Lyman,[3] thin crystalline quartz (0.2 mm) transmits as far as 1450A. Thicker pieces (2 mm) transmit to 1500A. The transparency limits for

[1] C. A. MACKAY, *Phil. Mag.*, **46**, 828 (1923).
[2] J. C. MORRIS, *Phys. Rev.*, **32**, 456 (1928).
[3] T. LYMAN, *Astrophys. Jour.*, **25**, 45 (1907).

clear fluorite from different sources vary tremendously. As no specimen, out of the many tested by him, transmitted farther into the ultra-violet than 1250A, we may conclude that this is the shortest wave-length transmitted by the best specimens of fluorite procurable. No substance is known which transmits as far into the ultra-violet as does fluorite. (Collodion films, about 10^{-5} cm thick, thin enough to show colors, are said to transmit more or less as far as the K emission line of carbon, 43A[1]. However, the possible applications of such films are no doubt limited by their fragility.) Another difficulty in the study of ionization of air and other gases by light is the fact that all solid surfaces emit photoelectrons copiously under the influence of short wave-length ultra-violet light, and hence it is very difficult to demonstrate the existence of a weak ionization in a gas when it is surrounded by surfaces capable of emitting photoelectrons readily. The difficulty has been evaded by streaming a gas past a window, through which the light is transmitted, into an ionization chamber shielded from the light. Negative ions in the stream may arise either from ionization of the gas or from a photoelectric effect at surfaces in the neighborhood of the window. Consequently one criterion for a genuine ionization of the gas is the presence of positive ions carried along by the stream.

Lenard[2] was the first to make systematic investigations on the ionization of air by light. He found that ultra-violet light from a spark discharged an electroscope whether it was charged positively or negatively. Since no light was allowed to fall on the electroscope itself, it was inferred that the air itself was ionized. Carbon dioxide and oxygen were ionized to about the same extent as air, coal gas was less ionized, while hydrogen was hardly ionized at all. Most of the experiments on air were made on the unfiltered air of the room; a few were made on filtered air. The active light was very strongly absorbed by the air. A very significant result is that the mobilities of the negative and positive ions obtained with unfiltered air were 3.13 cm/sec and 0.0015 cm/sec, respectively. The excessively low value of the mobility of the positive ion indicates that the conductivity observed is in all probability due to a photoelectric effect at the surfaces of dust particles, which, on losing an electron, are left positively charged and behave like a positive ion of very low mobility.[3] (Mobility experiments were not made with the filtered gases.) Both Lenard and C. T. R. Wilson[4] found that ultra-violet light has the property of producing nuclei in gases through which it passes. Wilson showed that, when intense ultra-violet light was

[1] M. F. Holweck, *Comptes Rend.*, **180**, 266 (1925).

[2] P. Lenard, *Ann. d. Phys.*, **1**, 486 (1900); **3**, 298 (1900).

[3] J. J. Thomson, "Conduction of Electricity through Gases," p. 254 (Cambridge University Press, 2d ed., 1906).

[4] C. T. R. Wilson, *Phil. Trans. Roy. Soc.*, **192**, 403 (1899).

directed into his expansion chamber, nuclei were created on which clouds could be produced with little or no expansion. Lenard found that these nuclei arose in some way from traces of impurities in the air. Whatever may be the nature of these nuclei, it is clear that they are solid or liquid particles and, as such, show a surface photoelectric effect. Thus, if positive charges appear in air as a result of illumination by ultra-violet light, it is necessary to show that they have the normal mobility of small ions before concluding that a real ionization of the air has occurred.

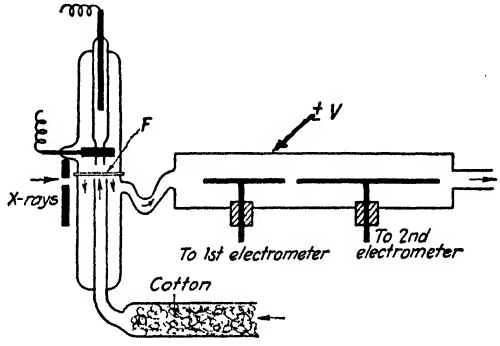

FIG. 7-15.—Apparatus for investigating photoionization in air.

Definite evidence that air itself, as distinct from dust particles or other nuclei suspended in it, can be ionized by ultra-violet light was obtained by Hughes.[1] The apparatus used is shown in Fig. 7-15. Ultra-violet light was obtained from a discharge in hydrogen, and passed through a fluorite window *F*. Air, filtered by cotton, was driven up against the fluorite window and then into an ionization chamber. Suitable bends in the connecting tube prevented any radiation from entering the ionization chamber. The presence of positive charges in the gas stream after passing the fluorite window was taken as evidence for ionization in the air. However, in view of Lenard's results, it was necessary to show that the positive charges were charged molecules, and not merely charges on dust particles which might have escaped the filter or on nuclei created in the air by the ultra-violet light. This was effected in two ways. Immediately after passing through the ionization chamber (now *without* a field to drive out ions), samples of the air exposed to the radiation were trapped in a Wilson expansion apparatus and tested. No drops or clouds were formed when the expansion was less than 1.25, showing the absence of nuclei larger than ordinary ions. The second test was effected by comparing the mobility of the positive ion produced by ultra-violet light with the mobility of that produced by X-rays. A beam of X-rays was directed through an opening in a lead screen in such a way

[1] A. L. HUGHES, *Proc. Camb. Phil. Soc.*, **15**, 483 (1910).

as to ionize the air just under the fluorite window. This insured that the ions were distributed throughout the stream of air in much the same way whether they were produced by light or by X-rays. An estimate of the mobility of the positive ion was obtained in the following manner. The two electrodes, shown in Fig. 7-15, were connected to separate electrometers. With the air streaming through the apparatus at a constant speed, the ratio of the charge measured by the second electrometer to that measured by both electrometers was plotted as a function of the positive

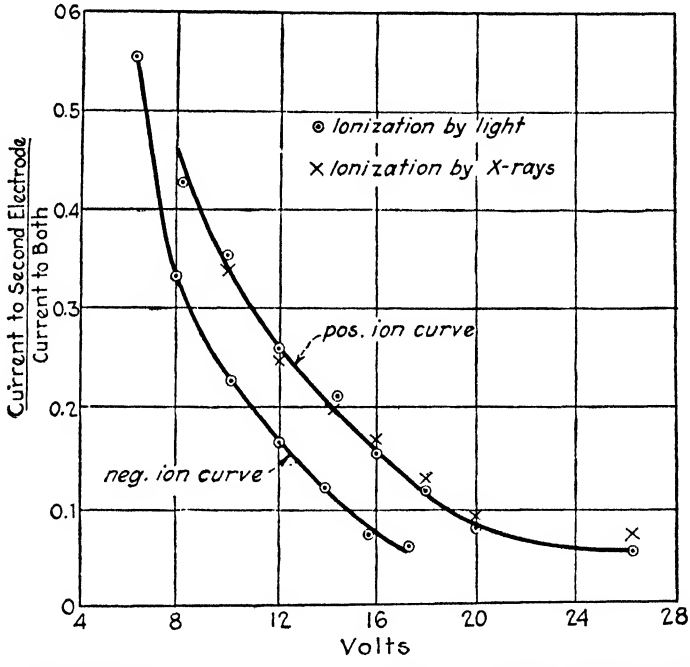

FIG. 7-16.—Comparison of mobilities of ions produced by X-rays in air with those of ions. produced by ultra-violet light.

potential applied to the cylindrical ionization chamber. The ratio diminishes steadily as the potential is increased, as of course there are fewer and fewer ions left to be driven to the second electrometer. For ions of high mobility the ratio should decrease more rapidly with the potential than for ions of low mobility. It was found that the ratio diminished in precisely the same way when ionization was produced by ultra-violet light as when produced by X-rays (Fig. 7-16). Consequently we are forced to the conclusion that in this experiment the positive ions, produced by ultra-violet light, are of precisely the same size as those produced by X-rays. This carries with it the inference that the conductivity of the air was due to a genuine ionization of the air molecules

themselves and not to charged dust particles or nuclei. The currents observed were of the order of 10^{-11} amp.

We can use the results of this investigation to determine approximately the wave-length of light at which ionization begins. Several thin plates of crystalline quartz (0.3 mm thick) were put in place of the fluorite window in the apparatus shown in Fig. 7-15. In no case was an ionization current as large as 10^{-15} amp observed. Lyman[1] had found that the transparency limit of thin crystalline quartz (0.2 mm thick) was constant for different specimens and was at 1450A. We may infer with a fair degree of certainty that the threshold for photoionization of air is at a shorter wave-length than 1450A. Lyman found that the transparency limits of clear colorless fluorite varied enormously from one specimen to another. His most transparent specimens transmitted to about 1250A. Out of many pieces of fluorite used for the window in these ionization experiments only one was found to transmit light capable of ionizing air. This specimen was unfortunately broken before its transparency limit could be tested. In view of Lyman's extensive study of the transparency of different specimens of fluorite it seems best to assume that the one piece of fluorite which transmitted the light which ionized air did not transmit beyond 1250A. This leads us to assign the threshold for the ionization of air to some wave-length between 1250A and 1450A and, in view of the large currents (10^{-11} amp) actually obtained, we may not be far wrong in tentatively concluding the threshold to be about 1350A.

Palmer[2] investigated the ionization of air and other gases with an apparatus somewhat similar in principle to that shown in Fig. 7-15. The chief difference was that between the hydrogen discharge tube and the gas whose ionization was being investigated there was an absorption cell, 1 cm long, bounded by fluorite windows whose transparency limits were known. The cell could be filled with oxygen to various pressures. From Lyman's investigations on the absorption of oxygen, the regions of the spectrum transmitted by the fluorite cell when filled with oxygen to various pressures may be tabulated as follows:

Pressure	Regions Transmitted
0	1250A to the visible
15 mm	1250A to 1350A and 1500A to the visible
40 mm	1250A to 1330A and 1600A to the visible
760 mm	1250A to 1270A and 1760A to the visible

It was found that, with the absorption cell empty, large ionization currents (of the order of 10^{-11} amp) were obtained in nitrogen and in oxygen when illuminated by ultra-violet light. The ionization was considerably

[1] T. Lyman, *Astrophys. Jour.*, **25**, 45 (1907).
[2] F. Palmer, *Phys. Rev.*, **32**, 1 (1911).

larger in nitrogen than in oxygen; for air an intermediate amount was obtained. The ionization diminished very rapidly as the pressure of oxygen in the absorption cell was increased up to atmospheric pressure. A very small amount of ionization was found in hydrogen due, perhaps, to impurities. As the table shows, some light of wave-length close to 1250A gets through even when the absorption cell contains oxygen at atmospheric pressure, and this might be sufficient to account for all the ionization observed. We can, therefore, only infer that the threshold for air is on the long wave-length side of 1250A, but no conclusions can be drawn as to how far it is from 1250A.

In 1911, Lenard and Ramsauer[1] published a detailed account of an elaborate investigation on the effects of ultra-violet light on air. As a source of light they used a powerful spark between aluminum rods. A quartz (or, in some cases, a fluorite) window separated the source of light from a stream of air which, after illumination, passed into an ionization chamber in which the conductivity, if any, could be measured. These authors made an extensive study of the part played by traces of impurities in the air. They found that many of these impurities (such as carbon dioxide, ammonia, vapors given off by cotton, rubber tubes, and glass wool), when illuminated by the intense radiation, gave rise to minute solid or liquid nuclei. These nuclei are photoelectrically active and, when they lose photoelectrons under the influence of the ultra-violet light, behave like ions of very large size. This accounts for the characteristic low mobility which appears time and again in Lenard and Ramsauer's results. The formation of these nuclei in the presence of ultra-violet light was finally completely avoided by strongly heating all the glass tubing in their apparatus and by freezing out impurities in the stream of air by passing it through a tube immersed in liquid air. Then, and only then, were they able to show that the ultra-violet light which passed through thin crystalline quartz could not ionize air. However, when a fluorite window was substituted for a quartz window, all other conditions remaining unchanged, they obtained a surprisingly large ionization. A test of the mobility of the ions showed that all of them were small—that is, of molecular size. Martin,[2] working in Lenard's laboratory, extended the same type of investigation to include air, oxygen, nitrogen, and carbon dioxide. The observed ionization currents under the same illumination (light from an aluminum spark through fluorite) were proportional to 135, 100, 155, and 152.

The results of Hughes, of Palmer, and of Lenard and Ramsauer are in satisfactory agreement in that in all three investigations true ionization of air appears to be produced only by light which can pass through

[1] P. Lenard and C. Ramsauer, *Sitz.-ber. d. Heidelberg. Akad. d. Wiss.*, 1910–1911.
[2] A. Martin (ed. C. Ramsauer), *Sitz.-ber. d. Heidelberg. Akad. d. Wiss.*, **10**, 1918.

certain selected pieces of fluorite. Further, in no case was it found that the light which passed through thin crystalline quartz could ionize air. The threshold of the ionization of air is therefore in between the transparency limits of thin quartz and of specially selected specimens of fluorite. Our discussion of Lyman's careful work[1] on the transparency limits of quartz and fluorite then leads us to conclude with reasonable certainty that ionization of air molecules by light sets in somewhere between 1250A and 1450A.

It is worth noting that Lenard and Ramsauer had much more trouble than had Hughes or Palmer in avoiding the formation of nuclei giving spurious effects. It is perhaps significant in this connection that the source of light used by Lenard and Ramsauer was far more intense than the sources used by the others. One may conjecture that these troublesome nuclei are not formed in appreciable numbers except as a result of very intense illumination.

7-11. Photoionization in Other Gases and Vapors.—Ludlam[2] failed to find any ionization in pure chlorine illuminated by light from an aluminum spark transmitted through fluorite, although the same light gave a measurable ionization in air. Ludlam and West[3] found that nitrogen, saturated with iodine vapor, became conducting when exposed to light passing through a fluorite window from a powerful aluminum spark. The effect was attributed to the iodine because it disappeared when pure nitrogen alone was used. (The absence of ionization in nitrogen is in disagreement with the work of Palmer and of Martin, unless we make the very reasonable assumption that the fluorite windows used by West and Ludlam did not transmit quite as far as the windows used by the others.) An absorption cell, 1 cm long, containing air, with fluorite windows placed between the source and the nitrogen-iodine mixture, caused the conductivity to disappear completely. In view of Lenard's results on the formation of solid or liquid nuclei by light in air not carefully purified, it is just possible that some such effect happened in the nitrogen-iodine mixture. An examination of the mobility of the positive ions should have been made to determine whether the positive ions were molecular in size, or of such a size as to indicate that they were charged nuclei. The ionizing potential of iodine as determined by Mackay[4] is 10 volts, and therefore it is just possible that light of the shortest wavelength, which the best specimens of fluorite can transmit, may be able to ionize an iodine molecule in one step.

Lenard and Ramsauer[5] found that carbon dioxide could be ionized

[1] T. Lyman, *Astrophys. Jour.*, **25**, 45 (1907).
[2] E. B. Ludlam, *Phil. Mag.*, **23**, 757 (1912).
[3] W. West and E. B. Ludlam, *Proc. Roy. Soc. Edin.*, **45**, 34 (1925).
[4] C. A. Mackay, *Phil. Mag.*, **46**, 828 (1923).
[5] P. Lenard and C. Ramsauer, *Sitz.-ber. d. Heidelberg. Akad. d. Wiss.*, 1910–1911.

by the light which had passed through a quartz plate. This indicates that the threshold is of longer wave-length than 1450A.

Stark[1] concluded that certain organic vapors (anthracene, diphenylmethane, α-naphthylamine, and diphenylamine) could be ionized by light from a mercury lamp (shortest wave-length probably 1849A). A voltage across the tube of only a few volts avoided any complication due to ionization by collision. An increase in the electric current through the tube with an increase in the pressure, over a more or less limited range, was accepted as a proof for the existence of a real photoionization of the vapor as distinct from a photoelectric effect at the surface of the electrodes. It is now doubtful whether these results indicate true photoionization. According to Gudden,[2] these vapors show a strong ultraviolet fluorescence which probably attains a maximum value at a certain pressure. This fluorescence, through its photoelectric action on the electrodes, would account for the observed effects.

Hughes[3] illuminated carbon disulphide (CS_2), zinc ethyl [$Zn(C_2H_5)_2$] and tin tetrachloride ($SnCl_4$) with ultra-violet light from a mercury lamp (shortest wave-length available probably 1849A). All three vapors absorbed the light powerfully, but no photoionization could be detected. The same light falling on a zinc plate produced a photoelectric current at least 10^6 times greater than the smallest ionization current which could have been detected.

An interesting field has been opened up by the discovery of Terenin,[4] who found that certain salt vapors, TlI, TlBr, TlCl, AgI, PbI_2, $PbCl_2$, and BiI_3, became conducting when exposed to ultra-violet light. The effects were large in the Tl compounds—diminishing from the iodide to the chloride—and small in the others. In Table 7-6, we have the threshold for photoionization, λ_0, its equivalent in volts (equivalent to the ionization potential), J_m, and the heats of dissociation (expressed in volts) of the neutral molecule D_m, and the ionized molecule D_i.

TABLE 7-6.—THRESHOLDS AND RELATED CONSTANTS FOR THALLIUM SALTS

Salt	λ_0	J_m	D_m	D_i
TlI	2140A	5.8	2.5	2.8
TlBr	2070A	6.0	3.2	3.3
TlCl	1860A(?)	6.7		

[1] J. STARK, *Phys. Zeits.*, **10**, 614 (1909).
[2] B. GUDDEN, "Lichtelektrische Erscheinungen," p. 231 (Julius Springer, 1928).
[3] A. L. HUGHES, *Proc. Camb. Phil. Soc.*, **16**, 375 (1911).
[4] A. TERENIN, *Phys. Rev.*, **36**, 147 (1930).

Values of D_m were taken from a separate paper. D_i was calculated by means of the formula

$$D_m + J_a = D_i + J_m.$$

The ionization potential corresponding to the threshold is within a few tenths of a volt of that of the Tl atom. Terenin believes that in the compound TlX the Tl behaves as if it were but little affected by the halogen X, and that it takes much the same amount of energy to remove an electron from Tl whether it is free or bound. The results cannot be explained as indicating a break-up of the molecule into Tl^+ and X^- because the threshold for this dissociation is quite different from that for photoionization.

7-12. Ionization in a Gas by Its Own Radiation.—Mohler[1] studied the photoionization in a gas illuminated by radiation from another portion of the same gas bombarded by electrons. At one end of a tube, electrons from a hot filament were driven at a controlled speed through a gas at low pressure. The ionization produced in the same gas at the other end of the tube was measured by the change produced in the space-charge limited current. (This method was described in Sec. **7-2.**) The novel feature in Mohler's arrangement was that there was nothing to absorb the radiation from the gas, except the gas itself. He found that the radiation from hydrogen produced no ionization in the hydrogen at the other end of the tube. This is as it should be, for none of the lines of hydrogen are "spark" lines; the energy in a quantum for any line of hydrogen must therefore necessarily be less than the energy required for ionization of the molecule.[2] For caesium and potassium vapors, argon, and neon, it is stated that the arc spectrum (*i.e.*, the spectrum which can be produced by impact of electrons of energy just below the ionizing potential) produces but little ionization in the same gas at the other end of the tube. (It is difficult to see why there should be any ionization at all, unless we admit the possibility of cumulative effects, or effects similar to those discussed in Sec. **7-7.**) On the other hand, strong photoionization effects were obtained when spark spectra were excited by electrons of higher energy. The spark spectrum includes lines for which the quanta have more energy than that corresponding to the ionizing potential of the normal atom. Hence ionization is to be expected. By noting the discontinuous changes in photoionization, Mohler was able to determine a number of critical potentials for the atoms concerned.

[1] F. L. Mohler, *Phys. Rev.*, **28**, 46 (1926); *Proc. Nat. Acad. Sci.*, **12**, 492 (1926).

[2] An investigation on somewhat similar lines has been carried out by J. Thomson (*Phil. Mag.*, **7**, 970 [1929]) who found that hydrogen could be ionized by its own radiation. However, the conditions were very different from those of Mohler. Thomson worked at atmospheric pressures and he used a discharge of several milliamperes between points as a source. If cumulative effects are possible in hydrogen, these conditions would undoubtedly favor them.

7-13. Nature of the Ionization in Air and Other Gases.—If we exclude Mohler's investigation, it will be noticed that the light which ionizes certain gases cannot have shorter wave-lengths in it than 1250A (transparency limit of fluorite). This carries with it the implication that the ionization potentials should be about 9.9 volts or less. For one vapor only—iodine—is there any possibility of regarding the ionization potential and the photoelectric threshold as in approximate agreement. The ionization potentials of oxygen, nitrogen, and carbon dioxide indicate that the photoionization thresholds for these gases should be 990A, 760A, and 860A, respectively, which are far removed from 1250A. It seems necessary therefore to assume that the observed ionization is a cumulative effect, in which absorption of the light first raises a molecule to an excited or metastable state corresponding to 9 or 10 volts energy. The ionization of such an excited molecule follows if its life is long enough to enable it to capture a second quantum, or to collide with another excited molecule. This interpretation would be supported if it could be proved that the ionization increased more rapidly than the first power of the intensity of the light. Further investigations in this field are badly needed.

7-14. The Direction of Ejection of Photoelectrons.—It has long been known that photoelectrons due to X-rays are ejected chiefly in a direction parallel to that of the electric force in the wave front, if we confine our attention to the plane perpendicular to the direction of the X-rays. Lawrence and Chaffee have recently published a short note[1] announcing the discovery of the same effect in K vapor, illuminated by polarized light. The number of electrons ejected in a direction parallel to the electric force was approximately double the number apparently ejected in the perpendicular direction. Those which appear to be moving in a direction at right angles to the electric force are probably scattered electrons. On making allowance for this scattering, the authors concluded that the angular distribution of the photoelectrons is in satisfactory accord with Sommerfeld's theory,[2] *viz.*, that the probability of ejection in any direction is proportional to the square of the cosine of the angle between this direction and that of the electric force in the wave front.

[1] E. O. Lawrence and M. A. Chaffee, *Phys. Rev.*, **36**, 1099 (1930). More recently a complete account of the work has appeared (M. A. Chaffee, *Phys. Rev.*, **37**, 1233 [1931]).

[2] For a discussion of this theory in connection with X-ray photoelectrons, see Sec. **11-9**.

CHAPTER VIII

PHOTOCONDUCTIVITY

We have hitherto discussed two types of photoelectric processes; (1) the surface effect in metals, and (2) the volume effect in gases. In the first type of effect, light releases electricity at the surfaces of solids or liquids into another medium, which is almost always a gas or a vacuum. In all such phenomena, it is known that the light penetrates a short distance into the substance, and it has been tacitly assumed that it liberates photoelectrons all along its path. The small fraction of these which escapes from the surface constitutes the photoelectric current in the ordinary surface photoelectric effect. These considerations lead one to expect effects which can be interpreted in terms of the separation of electrons throughout a given volume of matter when it is illuminated. In the case of gases and vapors, these effects constitute the well-known ionization of gases and vapors by light (Chapter VII). Since the existence of the separation of electrons throughout the illuminated volume can be revealed only by a current flow in an electric field, it is to be expected that the effect will always be completely masked in the case of conductors, and can be investigated only in the case of insulators, or possibly very feeble conductors. The change in the conductivity of selenium, when illuminated, has been known for over half a century, and has been the subject of many investigations. But in spite of all this work, there was, until recently, nothing known as to the fundamental photoelectric process underlying the photoconductivity of selenium. It was left to Gudden and Pohl to unravel the tangled problem of photoconductivity in solids in a series of masterly investigations. While all crystals probably conduct when irradiated by X-rays,[1] only certain classes of crystals, according to Gudden and Pohl, become conducting when illuminated by the visible or by the near ultra-violet part of the spectrum.

The term "photoconductivity" is a general one used to cover all changes of conductivity induced by illumination (apart, of course, from the ordinary changes of resistance due to heating). When the photoconductivity can be regarded as a true photoelectric effect (*e.g.*, when the current is proportional to the light intensity, when it starts and stops without lag, when it implies one electron separated for every $h\nu$ absorbed, etc.), it is convenient to describe it as the *volume photoelectric effect*, and to

[1] W. C. Röntgen, *Ann. d. Phys.*, **64**, 1 (1921).

call the current the *primary photoelectric current.* Gudden and Pohl made an important advance in the understanding of the mechanism of photoconductivity when they demonstrated that, in general, all sorts of secondary effects are superposed on the simple volume photoelectric effect. In many cases, of which selenium is an excellent example, the superposed secondary effects are so much greater than the fundamental primary photoelectric effect that they completely obscure it. Gudden and Pohl found that in certain insulating crystals it was possible to study the volume photoelectric effect by itself, and then, by suitable changes in the conditions, to follow the increasing secondary effects. In this way they obtained a clue to the interpretation of photoconductivity in cases where the secondary effects completely mask the fundamental photoelectric effect. We may anticipate the results by stating that the secondary effects are the result of a more or less temporary lowering of the natural resistance of the crystal, resulting from the changes produced by the passage of the primary current.

PHOTOELECTRIC EFFECTS IN SINGLE CRYSTALS

8-1. Measurements of Photoelectric Currents in Solids. Technique and Interpretation.—The method of experimentally investigating the photoelectric current is shown diagrammatically in Fig. 8-1. The crystal C is mounted between two electrodes which are in contact with

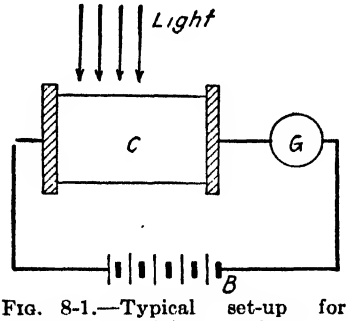

FIG. 8-1.—Typical set-up for photoconductivity experiments.

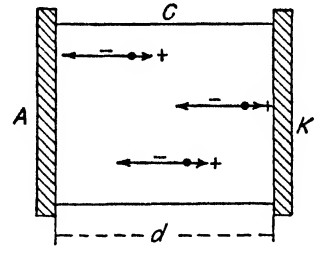

FIG. 8-2.—Motion of both negative and positive charges.

two opposite faces. B is a battery by means of which a suitable potential difference can be applied to the crystal. The galvanometer G can be used for measuring steady currents or, ballistically, for measuring quantities of electricity passing as a result of a flash of light on the crystal. When greater sensitivity is required, an electrometer can be substituted for the galvanometer.

The interpretation of the measurements has much in common with the interpretation of measurements on ionization of gases, but there is a difference in that we have to consider cases in which the charges do not travel all the way to the electrodes. Suppose that, under the influence

of the applied field, each negative charge moves a distance x_- in the crystal, and the corresponding positive charge moves a distance x_+ (Fig. 8-2). Let there be N such pairs of charges resulting from a flash of light on the crystal. Then the quantity of electricity indicated by the measuring instrument will be

$$Q = Ne\frac{x_- + x_+}{d}, \tag{8-1}$$

where d is the distance apart of the anode and cathode and e the charge.[1] If the negative and positive charges all move the whole distance towards their respective electrodes, then, since $x_- + x_+ = d$, we have

$$Q' = Ne. \tag{8-2}$$

This, of course, is the well-known formula in gases. If, on the other hand, the positive charges remain immovable, while the negative charges move right up to the anode (Fig. 8-3) then, since the average of x_- is $d/2$, we have

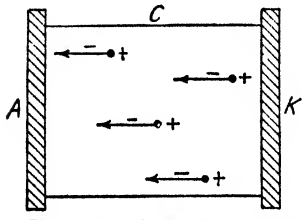

FIG. 8-3.—Negative charges move, positive charges stationary.

$$Q'' = \frac{Ne}{2}. \tag{8-3}$$

It should be noted that Eq. (8-3) implies a uniform production of charges throughout the whole space between the electrodes, while there is no such restriction for Eqs. (8-1) and (8-2).

As will be shown in the next section, the ballistic charge observed when single crystals are illuminated for a definite time increases with the applied potential, at first proportionally, then more slowly until saturation is reached. This behavior may be explained in the following manner:[2,3] Let us suppose that in the ideal crystal the electrons can move through the crystal lattice without hindrance under a very small field. In any actual apparently perfect crystal there will be departures from a perfect lattice due to submicroscopic cracks and imperfections and to foreign atoms embedded in the crystal, all of which act more or less as obstacles to the free movement of electrons. The smaller obstacles will be overcome when the electrons are driven by a small field, the larger obstacles will require a larger field to surmount them. Hence we may assume that, on the average, the distance x, moved through by an electron, is proportional to the applied field F. We thus have

$$x = kF = \frac{kV}{d}, \tag{8-4}$$

[1] W. FLECHSIG, *Zeits. f. Phys.* **46**, 788 (1927).
[2] B. GUDDEN and R. POHL, *Zeits. f. Phys.*, **16**, 170 (1923).
[3] W. FLECHSIG, *Zeits. f. Phys.*, **46**, 788 (1927).

where V is the applied potential, d the distance apart of the electrodes, and k a constant. If F_s and V_s be the saturation field and potential respectively, then

$$\frac{x}{d} = \frac{F}{F_s} = \frac{V}{V_s}. \tag{8-5}$$

We now suppose that x is an appreciable fraction of the distance d (Fig. 8-4). All the electrons released in II will reach the anode, while those

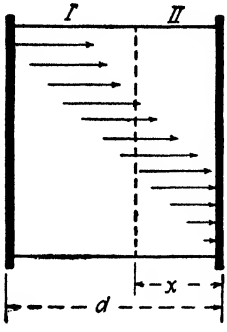

FIG. 8-4.

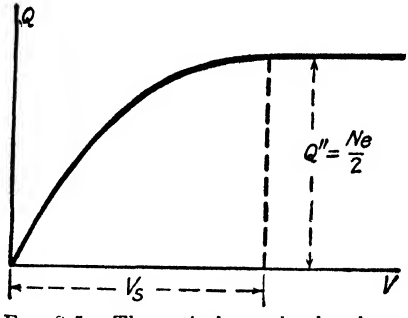

FIG. 8-5.—Theoretical coulomb-volta curve.

released in I will not do so. If N electrons are released uniformly over the whole volume, the contributions of I and II to the charge measured by the galvanometer in the circuit will be

$$\begin{aligned} Q &= Ne\frac{d-x}{d}\cdot\frac{x}{d} + \int_0^x \frac{Nedx}{d}\cdot\frac{x}{d} \\ &= Ne\frac{x}{d}\left[1 - \frac{x}{2d}\right]. \end{aligned} \tag{8-6}$$

Introducing Eq. (8-5), we have

$$Q = Ne\frac{V}{V_s}\left[1 - \frac{V}{2V_s}\right]. \tag{8-7}$$

This equation, which holds for $V \leq V_s$, is shown graphically in Fig. 8-5. The rising part of the curve is a parabola. The maximum value of Q, on putting $x = d$ in Eq. (8-6) is $Ne/2$, which is in agreement with Eq. (8-3). It is found that the current-potential curve for the photoelectric current through a diamond fits this parabolic relation excellently.[1] Flechsig[2] tests the implications of this theory in a somewhat different manner and concludes that the assumptions are adequate. On putting $x = d$, and $V = V_s$ in Eq. (8-4) we find that

$$V_s = \frac{d^2}{k}, \tag{8-8}$$

[1] B. GUDDEN and R. POHL, *Zeits. f. Phys.*, **17**, 331 (1923).
[2] W. FLECHSIG, *Zeits. f. Phys.*, **46**, 788 (1927).

which implies that the potential necessary for saturation increases as the square of the thickness of the crystal.

It will be noticed that, at potentials far below the saturation potential, the current-potential relation is a linear one as in Ohm's law.

In the foregoing, it is to be assumed, of course, that the quantities of electricity moved are sufficiently small so that the positive charges left at the places from which the electrons are released do not build up a space charge of sufficient magnitude to make the real field within the crystal differ appreciably from the applied field. (In actual experiments, as will be seen later, very appreciable space charges are frequently built up.)

While these current-potential curves in crystals resemble those obtained in ionized gases, it should be noted that recombination of positive and negative charges plays no part in the theory given here. In gases, because of recombination, the greater the density of ionization, the higher is the value of the potential necessary for saturation. The current-potential curves for crystals are independent of the density of ionization, and so there is no evidence for the existence of recombination between charges of opposite signs within a crystal. Additional support for this statement is the fact that the current is found to be proportional to the light intensity at all potentials, a result which does not hold in gases.

It is desirable to point out the connection between conduction and polarization in a crystal in which a volume photoelectric effect is induced. A permanent current can be maintained through a crystal if the negative charges (electrons) can travel all the way to the anode. (The applied field must, of course, be sufficiently large to overcome the opposing field of the positive space charge due to the positive charges left, unless they themselves drift towards the cathode.) If, on the other hand, the displacements x_- and x_+ are of atomic dimensions, we have no genuine conductivity, in the sense that real charges are given up to the electrodes, but we do have a "polarization" set up in the medium. We can still have a polarization in a wider sense if the distances moved through are many times larger than atomic distances but yet considerably smaller than d. The measuring instrument will continue to indicate the flow of a (displacement) current, as more and more negative and positive charges are separated until the opposing field due to polarization within the crystal builds up and annuls the applied field. There is evidently no clear-cut division between conductivity and polarization in the wider sense used here. The distinction reduces merely to a difference in the length of path along which the electrons can travel in the crystal.

If, in Eq. (8-1), we can determine N in some independent way, then a measurement of Q at once leads to a determination of the average separation $(x_- + x_+)$ between two corresponding charges. In view of the quantum equivalence established for diamond and zincblende when the charges are driven all the way across the crystal, it seems justifiable in many cases to *assume* that N is given by the number of absorbed quanta which, in turn, is given by the total amount of energy absorbed. (An illustration of this will be found in Sec. 8-8.)

Other explanations of the mechanism of photoelectric currents have been preferred by Joffé.[1] Ohm's law is explained by the very natural assumption that the velocity of the electron is proportional to the electric field as in metals and in electrolytes, a view which Joffé maintains is less forced than that of Gudden and Pohl. On the other hand, Joffé offers no picture of how saturation is attained, nor does he give a quantitative expression for the current-potential curve (Fig. 8-5).

8-2. Separation of the Primary Photoelectric Currents and Secondary Currents.—A great advance was made in the understanding of the nature of photoconductivity when Gudden and Pohl demonstrated that the observed current was almost always the sum of two distinct currents. The first current, the primary photoelectric current, is directly due to the motion of charges released throughout the illuminated volume by a photoelectric process. The secondary current, on the other hand, comes about from a reduction in the resistance of the material as a result of the flow of the primary current. It is therefore in no sense a photoelectric effect, it is merely initiated in this particular case by an underlying photoelectric effect. Under carefully controlled experimental conditions, the primary photoelectric current, unaccompanied by a secondary current, may be investigated. In ordinary selenium cells, on the other hand, the secondary current is so very much larger than the primary photoelectric current that the latter is completely obscured.

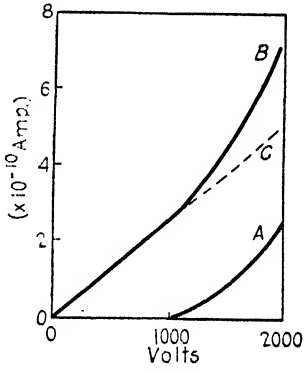

Fig. 8-6.—Dark current in zincblende (ZnS). Area, 1 cm²; thickness, 1 mm.

The separation of the secondary current from the primary photoelectric current may be illustrated from the work of Gudden and Pohl on zincblende.[2] Curve A (Fig. 8-6) shows the initial conductivity of zincblende (a very clear crystal with a faint yellowish tinge) in the *dark*, when mounted between water electrodes 1 cm² in area. The natural resistance is clearly dependent on the electric field. After the current has been flowing for a time, the current-potential curve changes to the curve OB. The inference is that invisible conducting fibers, perhaps metallic, have bridged over from one electrode to the other. The conductivity of these fibers is ohmic, and clearly the current-potential curve is the sum of a new straight line OC and the initial curve A. Following Tubandt,[3] Gudden and Pohl interpret this effect to mean that the

[1] A. F. Joffé, "The Physics of Crystals," Chap. XIII (McGraw-Hill Book Company, Inc., 1928); also P. Pringsheim, "Fluorescenz und Phosphorescenz," p. 185 (Julius Springer, 1928).

[2] B. Gudden and R. Pohl, *Zeits. f. Phys.*, **6**, 248 (1921).

[3] C. Tubandt, *Zeits. f. Anorg. Chem.*, **110**, 196 (1920); **115**, 105 (1920); **117**, 48 (1921).

conductivity is electrolytic. (Joffé states that all transparent crystals conduct electrolytically, that is, by the transfer of matter through the crystal.[1]) The clear crystal of zincblende was illuminated by monochromatic light of constant intensity, for known intervals of time, and the curves in Fig. 8-7 were obtained. It is evident that, for the lower voltages, the quantity of electricity released by the light is strictly proportional to the time of illumination. For the higher voltages, the curves become concave upwards, indicating the onset of a secondary current. On the tentative assumption that the secondary current I_s builds up (at first at all events), proportionally to the time t, we find that the total quantity of electricity

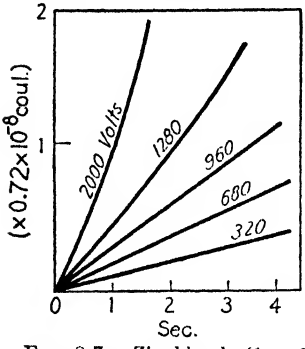

FIG. 8-7.—Zincblende (1 cm² × 1 mm). Illuminated by 4050A. Light intensity 0.264 × 10^{-7} cal/sec cm².

$$Q = I_p t + I_s t = I_p t + kt^2, \tag{8-9}$$

where I_p is the primary photoelectric current, and k a constant defined by $I_s = kt$. By means of Eq. (8-9), Fig. 8-8 was derived from Fig. 8-7. It will be seen that the primary current becomes saturated at about 1600 volts (16,000 volts/cm), while the secondary current, calculated for 1 sec, is remarkably like the electrolytic current A in Fig. 8-6, in its depend-

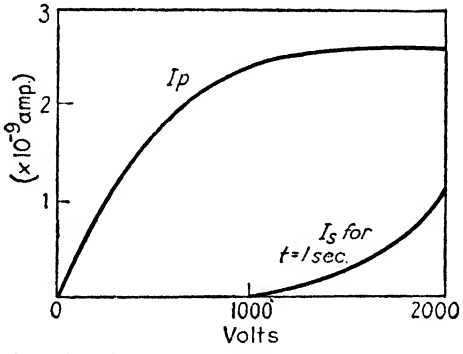

FIG. 8-8.—Primary photoelectric current and secondary current; dependence on voltage.

ence on the applied field. To establish the result that the primary photoelectric current is proportional to the intensity of the light, the quantities of electricity, measured ballistically by a galvanometer, were determined in terms of the intensity and the time of illumination. The results are given in Fig. 8-9. Assuming that these curves fit the parabolic Eq. (8-9), it was possible to construct Fig. 8-10 from Fig. 8-9. This shows that the primary photoelectric current I_p is strictly propor-

[1] A. F. JOFFÉ, *loc. cit.*, Chap. IX.

tional to the intensity of the light, while the secondary current I_s (averaged over an arbitrary standard time $t = 1$ sec) increases rapidly with the

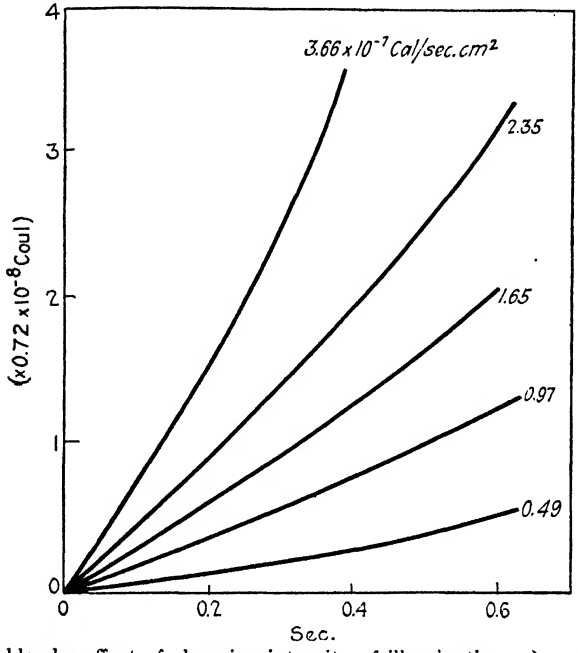

FIG. 8-9.—Zincblende; effect of changing intensity of illumination. $\lambda = 4360$A; applied voltage, 1600 volts (saturation).

intensity of the light. This is quite in accord with the view that the secondary current increases as the resistance of the crystal diminishes owing to cumulative changes produced in it by the flow of the primary current. We see that the primary photoelectric current fulfills all the requirements laid down for a real photoelectric effect. Fuller discussion of the secondary current will be given in Sec. **8-16.**

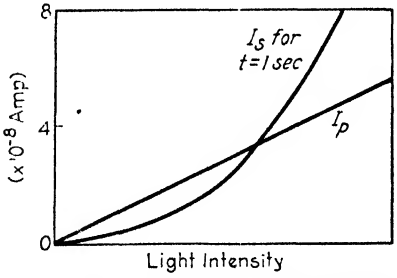

FIG. 8-10.—Primary photoelectric current and secondary current; dependence on light intensity.

From these results we learn that to investigate the primary photoelectric current itself, uncomplicated by the presence of a secondary current, it is necessary to produce as little disturbance in the crystal as possible. This, in practice, is effected by cutting down the intensity of light and the time of illumination to the lowest possible values. Also it is found that the primary photoelectric current is best studied in large flawless crystals.

8-3. The Primary Photoelectric Current.—The primary photoelectric current is proportional to the intensity of the light whether the current be saturated or unsaturated. This is illustrated in Fig. 8-11 for the case of zincblende.[1] The current-potential curve, leading up to saturation is

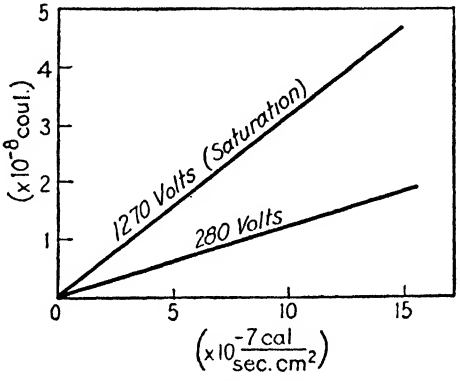

FIG. 8-11.—Proportionality between quantity of electricity separated and intensity. Zincblende (25 mm² × 1.3 mm); λ = 4360A.

shown in Fig. 8-12. It will be seen that the curve is the same whether the primary photoelectric current is produced by 3340A or by 4360A. The light intensities are so adjusted that the same saturation current is produced in each case. The significance of these results lies in the fact that light of wave-length 4360A diminishes in intensity to 0.88 on passing

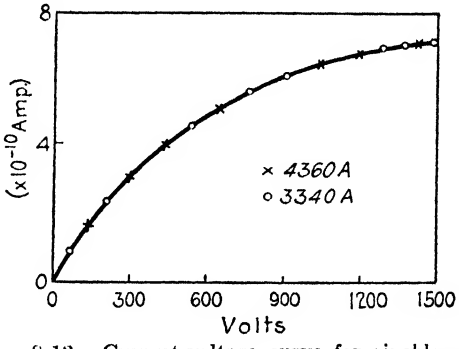

FIG. 8-12.—Current-voltage curve for zincblende.

through 1 mm, while light of wave-length 3340A is diminished to 10^{-10} on traversing the same distance. Consequently, the density of ionization within the region to which it is limited, is far greater with 3340A than with 4360A. As was indicated in Sec. **8-1**, the ease of attaining saturation in gases is conditioned by recombination between the positive and negative ions; the lower the density of ionization, the lower the potential at which saturation is obtained. The fact that, in crystals, saturation is

[1] B. GUDDEN and R. POHL, *Zeits. f. Phys.*, **17**, 331 (1923).

reached at the same potential whether the ionization is concentrated in a small fraction of the volume or is distributed over the whole of it is a strong argument for the view that recombination between positive and negative charges plays no appreciable part in determining the shape of the current-potential curve.

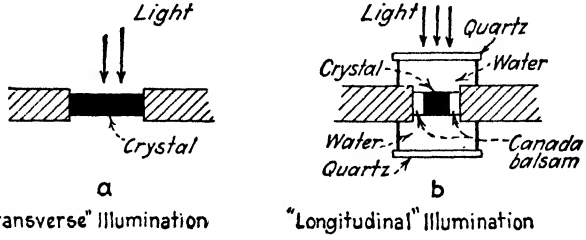

FIG. 8-13.

Similar results were obtained for a cubical diamond. For "transverse" illumination the diamond was mounted between metal electrodes as in Fig. 8-13*a*, while for "longitudinal" illumination, it was mounted between water electrodes as in Fig. 8-13*b*. The ballistically measured

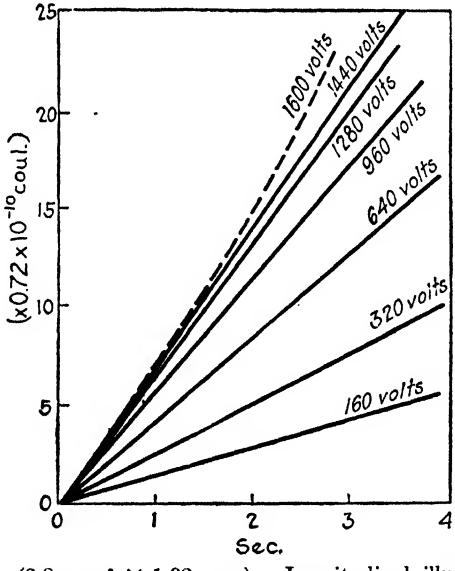

FIG. 8-14.—Diamond (2.8 mm² × 1.02 mm). Longitudinal illumination, λ = 3130A. Light intensity, 1.33 × 10^{-8} cal/cm² sec.

quantities of electricity passing through the diamond as a function of the time of illumination and of the applied potential are given in Fig. 8-14.[1] It will be noticed that up to 1440 volts the amount of electricity registered is strictly proportional to the time of illumination. With 1600 volts, there is an indication of a secondary current for illumination periods

[1] B. GUDDEN and R. POHL, *Zeits. f. Phys.*, 7, 69 (1921).

exceeding about 1 sec. The derived current-potential curves for diamond were quite similar to those for zincblende (Fig. 8-12). The results were the same whether the illumination was "transverse" or "longitudinal." It is to be noted (though it was not explicitly stated by Gudden and Pohl) that the shape of the current-potential curves for zincblende and diamond fit the parabolic curve given by the theory of Sec. **8-1.** Thus the departure

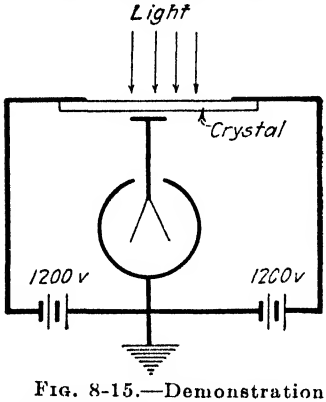

FIG. 8-15.—Demonstration of positive space charge within a crystal.

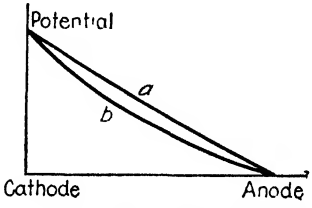

FIG. 8-16.—Potential distribution in crystal in Fig. 8-15. (*a*) Before illumination; (*b*) after illumination.

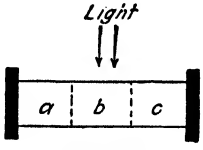

FIG. 8-17.

from saturation is to be interpreted as indicating that the photoelectrically released electrons travel only a part of the path to the anode, while saturation indicates that the field is sufficiently high to drive all the electrons to the anode.

For each electron released and shifted more or less on its way to the anode, a corresponding positive charge must be left behind. Thus a positive space charge should be built up within the crystal. This was shown in a large, uniform, almost colorless crystal of zincblende, mounted between tin electrodes and illuminated transversely.[1] The applied potential 2400 volts (field 3000 volt/cm), was far below saturation and also below that necessary to evoke secondary currents. A probe connected to an electroscope was used to explore the electrical state of the crystal (Fig. 8-15). On illumination, no matter where the probe was, it showed a positive charge, *i.e.*, the linear field *a* before illumination takes the shape *b* after illumination (Fig. 8-16). (Evidence for the formation of a negative space charge in a crystal due to the accumulation of photoelectrons will be found in Sec. **8-15.**)

When a flawless crystal of zincblende was illuminated only over the middle third of the distance between the electrodes as in Fig. 8-17, the current flowing under a certain illumination was over one hundred times what it had been in the dark.[2] Had the effect of the light been merely to alter the resistance of the illuminated portion, the current could only, at the most, have increased to 1.5 (due to a resistance change from $[a + b + c]$ to $[a + b]$; a, b, c, being all equal in the dark). This fact speaks in favor of an explanation in terms of a photoelectric effect in b, and also strongly suggests that

[1] B. GUDDEN and R. POHL, *Zeits. f. Phys.*, **7**, 69 (1921).
[2] B. GUDDEN and R. POHL, *Zeits. f. Phys.*, **7**, 65 (1921).

a crystal lattice offers no hindrance to the motion of electrons through it. A lattice insulates in the dark because there are no free electrons in it, not because it will not allow them to move in it. This is confirmed by Lenz's discovery[1] that electrons driven into a crystal by electronic bombardment will move within it under a suitable

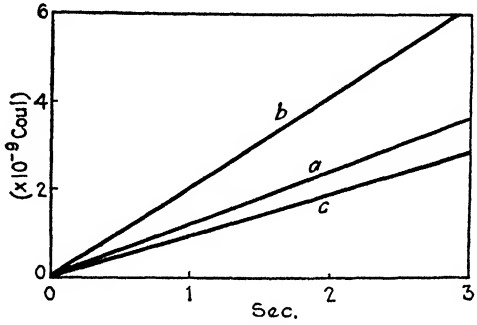

FIG. 8-18.—Effect of infra-red light. Diamond (3 mm² × 1 mm); 1200 volts (nearly saturation). (*a*) Illumination with 3130A alone (2.16×10^{-6} cal/sec cm²). (*b*) Illumination with 3130A and infra-red light (latter = 5×10^{-2} cal/sec cm²). (*c*) Illumination with infra-red light alone, *after* illumination with 3130A.

field. Still another fact supporting the photoelectric explanation of the primary current is the "addition law." No matter whether the crystal is illuminated locally (as at *b*) or uniformly over the whole side (as over $a + b + c$), the same photoelectric current passes for the same amount of light absorbed. (Because of the complications arising from space charges, it is necessary, in order to demonstrate this addition law,

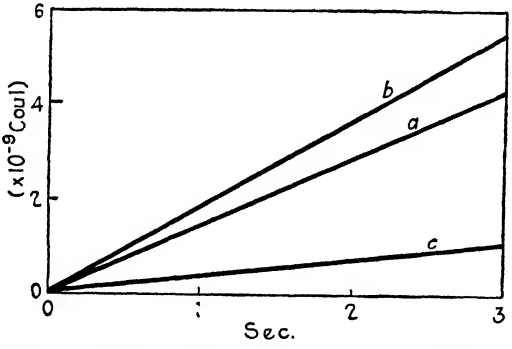

FIG. 8-19.—Effect of infra-red light. Zincblende (25 mm² × 1.2 mm); 900 volts (*a*) Illumination with 4360A (6×10^{-8} cal/cm² sec). (*b*) Illumination with 4360A and intense infra-red light (latter = 4×10^{-4} cal/cm² sec). (*c*) Illumination with infra-red light alone, *after* illumination with 4350A.

to use small light intensities and to obtain saturation currents. Moreover, a very good crystal, free from flaws and photoelectrically uniform, is necessary.)

8-4. Effect of Red and Infra-red Light.—In most crystals, the primary photoelectric current results only from illumination by blue or ultra-violet light. Strong red or infra-red light produces no photoelectric effect, or to be more exact, the photoelectric effect which

[1] H. LENZ, *Ann. d. Phys.*, **77**, 449 (1925).

it produces is negligibly small in comparison with that produced by the shorter wave-lengths. If, however, a crystal is illuminated simultaneously with strong red and infra-red light together with the light which calls out a photoelectric effect, then the photoelectric current is increased, sometimes to practically double its value.[1] Figures 8-18 and 8-19 illustrate this effect for diamond and zincblende, respectively. For diamond, illuminated only by 3130A, the quantities of electricity measured for different times of illumination are given on the line *a*. When, however, the diamond is simultaneously illuminated by intense red or infra-red light, the quantities measured lie on the line *b*. Gudden and Pohl take the view that the long wave-length light makes it possible for the positive charges, previously practically immobilized in the crystal, to move towards the cathode. (This should double the measured current in accordance with Eqs. [8-2] and [8-3].) Support for this view is afforded by measurements made in intense red light *after* measurements had been made under illumination by 3130A alone. The values on the line *c* were then obtained. On the theory given, the values on the line *c* correspond to the liberation by red light of the positive charges left after the electrons had moved away to the anode. The sum of the ordinates of *a* and *c* amount to approximately 90 per cent of *b*. Corresponding results for zincblende are shown in Fig. 8-19. Here the results indicate a somewhat slow spontaneous motion of the positive charges towards the cathode in the absence of red light. Values on the line *c* are obtained when intense red light is turned on 10 sec after illumination by 4360A alone. If the experiments are repeated, but with the interval extended to 40 sec, no current is to be found, showing, on this theory, that in 40 sec all the positive charges have spontaneously shifted to the cathode.

The theory receives further support from the results for diamond, given in Table 8.1.[2] These results imply that, in this diamond, or under

TABLE 8-1.—PHOTOELECTRIC CURRENTS IN A DIAMOND

Quantity of electricity due to illumination by 4360A alone	Quantity of electricity due to illumination by intense infra-red light, *after* illumination by 4360A alone
3.75×10^{-10} coul	3.63×10^{-10} coul
3.38	3.26
3.38	3.38
2.75	2.75
2.00	2.03

[1] B. GUDDEN and R. POHL, *Zeits. f. Phys.*, **16**, 174 (1923).
[2] B. GUDDEN and R. POHL, *Zeits. f. Phys.*, **20**, 14 (1924).

the conditions now obtaining, the positive charges have no tendency to move spontaneously at all. Hence when they are made free by infra-red light, they contribute just as much to the measured charge as did the electrons released by 4360A. In fact, even after several hours it was found that an appreciable part of the positive charge remained in the diamond. (A case is recorded in which a positive charge could be detected after a week.) On the other hand, the positive charges in zincblende disappear in less than a minute. Kurrelmeyer[1] could not detect any positive charges in a sulphur crystal by illumination with long wave-length light after a photoelectric effect had been observed with short wave-length light.

It is not to be assumed that a positively charged atom as such moves bodily through the crystal; it is much more likely that it is the *location* of the positive charge which moves towards the cathode, perhaps by the positive charge capturing an electron from its neighboring atom next towards the cathode, and by the repetition of this process atom by atom. Further consideration of the process will be deferred to the next section. Meanwhile we record that Gudden and Pohl call the current observed when the positive charges are immobilized, the "negative part of the primary photoelectric current," while the current which can be attributed to the shift of the location of the positive charge towards the cathode is called the "positive part of the primary photoelectric current." We shall use the shorter terms "electron primary photoelectric current," and "positive primary photoelectric current," when it is necessary to distinguish between them.

Now it will be seen that there is a great advantage in flooding the crystal with red or infra-red light when studying the photoelectric effect due to shorter wave-lengths. The full current, including the positive primary photoelectric current as well as the electron primary photoelectric current, will be registered. Besides this, infra-red light eliminates the troublesome space charges.

8-5. Effects at the Electrode Boundaries of Crystals.—Evidence as to what happens to the charges when they reach their respective electrodes is afforded by the following experiment:[2] A crystal of zincblende between two metal electrodes was illuminated by monochromatic light (4360A) and the quantities of electricity measured for small intervals of time. After each observation, the applied field was removed and the crystal again illuminated by the same light. It was found that a current in the *reverse* direction was obtained. Clearly, charges were built up on the faces of the crystal next to the electrodes, and, when the applied field was removed, these charges produced a field in the opposite direction as revealed by the reverse current. Complete equality of the currents

[1] B. Kurrelmeyer, *Phys. Rev.*, **30**, 901 (1927).

[2] B. Gudden and R. Pohl, *Zeits. f. Phys.*, **16**, 176 (1923).

is observed only for small values of the charges (Fig. 8-20). From the point of departure A from perfect reversibility it is estimated that when

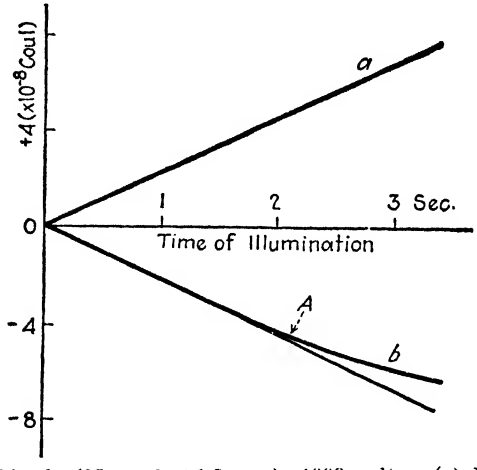

FIG. 8-20.—Zincblende (25 mm² × 1.2 mm); 1000 volts. (*a*) Effect due to 4360A in an electric field. (*b*) After effect due to illumination by 4360A without an electric field.

the surface density of charge exceeds 1.8×10^{-8} coul/cm² the charges begin to pass from the crystal into the electrodes.

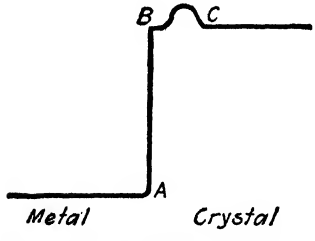

FIG. 8-21.—Energy curve at metal-crystal boundary.

With crystals of Class I,[1] *e.g.*, diamond and zincblende, Gudden and Pohl have always been able to obtain steady currents (*i.e.*, not falling to zero as time goes on) indicating that the charges certainly go into the electrodes.[2] On the other hand, they find that in Class II crystals, *e. g.*, colored rocksalt, the current ultimately vanished unless the whole distance between the electrodes was illuminated.

Kurrelmeyer[3] investigated the same point in a sulphur crystal and inferred that charges began to pass through into the electrodes when the surface density reached the value of 4×10^{-12} coul/cm², which is low in comparison with that cited for zincblende. Herzfeld[4] points out that this peculiarity in the passage of electrons from the crystal to the electrode in contact with it indicates that we must picture the energy curve of an electron in the vicinity of a boundary between a metal and a crystal as in Fig. 8-21. The discontinuity AB represents the energy with which the conduction electrons are bound in the metal (*i.e.*, the work function of the metal) while the small hump C seems

[1] A fuller discussion of the classes of crystals is given later in Sec. **8-14**.

[2] B. GUDDEN and R. POHL, *Zeits. f. Phys.*, **20**, 14 (1924).

[3] B. KURRELMEYER, *Phys. Rev.*, **30**, 901 (1927).

[4] K. F. HERZFELD, *Phys. Rev.*, **34**, 791 (1929).

necessary to account for the failure of the electrons to pass freely from the crystal into the metal. (The curve is quite similar to the energy curves for a metal-vacuum interface discussed in Chapter VI.)

8-6. Crystal Imperfections.—The view that departures from perfect regularity in a crystal hinders the motion of electrons is well illustrated by an observation of Gudden and Pohl,[1] in which a large crystal of zincblende was mounted between metal electrodes (Fig. 8-22). When the clearest portion of the crystal was between the electrodes a certain initial current was obtained. On turning the crystal so that the crack *SS*, into which iron sulphate had penetrated, lay between the electrodes, the initial current was diminished to about 25 per cent. Moreover, when the crack was between the illuminated strip and the anode, the diminution was greater than when it was between the illuminated strip and the cathode, in accordance with the view that the electrons move towards the anode while the positive charges undergo a considerably smaller shift back towards the cathode.

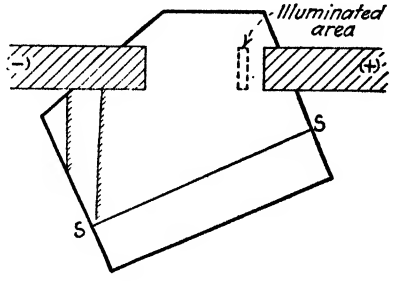

FIG. 8-22

Gudden[2] mentions that, in point-by-point illumination of a crystal of zincblende in which there are alternate strips of clear and colored portions, only the clearest spots showed photoconductivity. The view taken is that the photoelectric effect itself is not suppressed but that the electron movements are greatly interfered with in the colored parts.

These experiments give the clue to the more or less complete suppression of the primary photoelectric current in imperfect crystals. Among these we may class crystals with repeated twinnings, tablets of compressed powdered crystals, and some glasses which may be regarded as a collection of tiny crystals welded together. Each small crystal is a good photoelectric conductor in itself, but each boundary is an obstacle and has a work function which has to be overcome in order to drive the electron through.

8-7. The Primary Photoelectric Current in Selenium and Sulphur.—Although the photoconductivity of selenium has been investigated for over half a century and the results published in over 1500 papers, there is but one recorded study of the real primary photoelectric current in selenium under conditions which secure the absence of the very large secondary currents. It is therefore very satisfactory to find that, underlying all the amazing complications encountered in the study of photocon-

[1] B. GUDDEN and R. POHL, *Zeits. f. Phys.*, 7, 65 (1921).
[2] B. GUDDEN, "Lichtelektrische Erscheinungen," p. 155 (Julius Springer, 1928).

ductivity in selenium, there is a simple photoelectric process. Gudden and Pohl found that by using a single crystal of selenium (the red insulating variety) and short times of illumination the primary photoelectric effect could be isolated from secondary effects.[1] In Fig. 8-23, we see that the primary photoelectric current is directly proportional to the time of illumination (for 6400A and 9000A, only when the interval is small). The wave-length 6400A is strongly absorbed and the absorption diminishes steadily towards longer wave-lengths. Thus 9000A is to selenium roughly what red light is to diamond or zincblende, whose absorption becomes great in the ultra-violet. For the relatively short wave-length 6400A we note the slight diminution of current due to the rising space charge. For 9000A we observe the slight increase of current with the time which is to be attributed to the increasing mobility of the positive charges as their density increases. A strict proportionality is found between the primary photoelectric current and the intensity of the light. For constant illumination, the photoelectric current is proportional to the applied field up to 4000 volts/cm, there being no indication of approaching saturation. Results practically identical in characteristics with those just described for selenium have been obtained with stibnite (Antimonglanz) by Voight.[2]

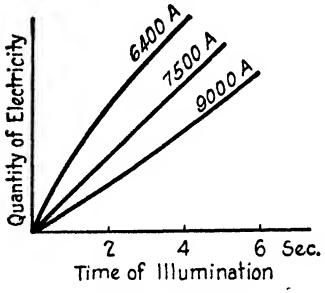

FIG. 8-23.—Primary photoelectric effect in selenium (a single red insulating crystal).

Joffé found that the conductivity in a pure single crystal of sulphur could be increased a millionfold by illumination.[3] In many respects, the photoelectric conductivity in sulphur crystals resembles that in selenium according to Kurrelmeyer.[4] The current is proportional to the intensity of the light, the range of variation being from 1 to 100. The current is strictly proportional to the field up to 15,000 volts/cm (the highest used). Saturation therefore requires a higher field, perhaps a much higher one. The photoelectric yield per unit intensity of incident light increases as we go from the red to the blue; at 4700A it drops almost abruptly. When we note it is in this region that the optical absorption begins to increase very rapidly, we see a strong resemblance to the behavior of diamond and zincblende (Sec. **8-8**). The positive primary photoelectric current appears to flow simultaneously with the electron primary current, for no current is observed on flooding a sulphur crystal with red light after it has been illuminated with blue light. However,

[1] B. GUDDEN and R. POHL, *Zeits. f. Phys.*, **35**, 243 (1925).
[2] K. H. VOIGHT, *Zeits. f. Phys.*, **57**, 154 (1929).
[3] A. F. JOFFÉ, *loc. cit.*, p. 134.
[4] B. KURRELMEYER, *Phys. Rev.*, **30**, 901 (1927).

the diminution of the photoelectric current to a final value of about one-third of its initial value points to the building up of a space charge which partly compensates the applied field.

8-8. Quantum Equivalence.—Gudden and Pohl proved that, under favorable conditions, the absorption of each quantum of radiation capable of calling out a photoelectric effect sets free one electron.[1] Thus if N quanta are absorbed, a charge Ne should be registered in the measuring instrument, provided, of course, that the applied potential is sufficiently high to produce saturation and provided that infra-red light is used to

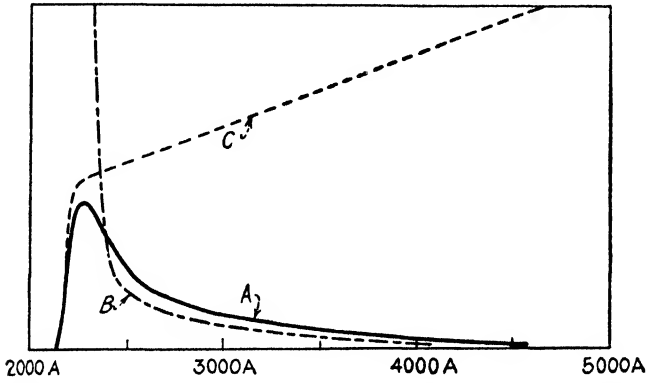

FIG. 8-24.—Quantum equivalence in a diamond. *A*. Photoelectric yield referred to *incident* light. *B*. Absorption coefficient. *C*. Photoelectric yield referred to *absorbed* light.

give mobility to the positive charges. Since the absorbed energy is $Nh\nu$, the electrical "yield" should be $Ne/Nh\nu = \lambda \times$ const. The yield should therefore *increase* proportionally to the wave-length. If λ be measured in Angstroms, the yield should be $3.4 \times 10^{-4} \times \lambda$ coul/cal. For the wave-length 3000A, this turns out to be 1.02 coul/cal.

To test this hypothesis experimentally, Gudden and Pohl used a very clear homogeneous diamond 1.02 mm thick. They measured the quantity of electricity separated in terms of the energy of the *incident* light for different wave-lengths (Fig. 8-24, curve A). Then, making use of Peters' determination[2] of the absorption coefficients of the diamond (curve B) they computed the quantity of electricity separated per calorie of *absorbed* light, in other words, the electrical "yield." This gives the curve C in Fig. 8-24. It is evident that the electrical yield is proportional to the wave-length and, moreover, its absolute value is in accordance with theory. Working backwards, Gudden and Pohl computed h to be about 7×10^{-27} erg sec. Similar results were obtained with a very clear piece of zincblende.

[1] B. GUDDEN and R. POHL, *Zeits. f. Phys.*, **17**, 331 (1923).
[2] F. PETERS, *Zeits. f. Phys.*, **15**, 358 (1923).

The fact that, whenever it is impossible to attain saturation in some crystals, the yield in the primary photoelectric current is always much less than the theoretical value, is in accord with the view that if saturation could be secured, a quantum equivalence might be obtained. In crystals containing impurities it is always possible that much of the light is absorbed by the foreign matter in a way that contributes nothing to the photoelectric effect. Gyulai found that with colored rocksalt crystals saturation could not be obtained with the potentials available.[1] On the view that departure from saturation is due to the electrons moving but a fraction of the thickness of the crystal, and assuming that the ratio of this fraction to the whole thickness is equal to the ratio of the observed yield to the theoretical quantum yield, he was able to estimate that in a colored rocksalt crystal the electrons traveled about 0.0003 cm in a field of 2000 volts/cm. For some time there seemed to be no indication of approaching saturation in the class of crystals to which colored rocksalt belongs. However, Flechsig[2] succeeded in cutting a crystal of rocksalt only 0.1 mm thick, and obtained a saturation current through it with a field of about 40,000 volts/cm. It did not appear possible to determine the absorption of light in this crystal and so to test the truth of the quantum-equivalence hypothesis. But in the absence of evidence to the contrary, it seems reasonable to assume that quantum equivalence exists.

The falling off of the primary photoelectric current when the absorption of the diamond or other crystal becomes high is an unsolved puzzle. The absorption coefficient of the diamond increases rapidly and steadily on the short wave-length side of 2500A, but the primary photoelectric current drops almost abruptly to zero at 2250A (Fig. 8-24).

In the surface photoelectric effect the yield diminishes rapidly to zero as one approaches the threshold from the short wave-length side. In the volume photoelectric effect, on the other hand, the yield actually increases linearly as we go towards longer wave-lengths, thus suggesting that there is no such thing as a threshold for this effect. The yield increases with the wave-length right up to the point at which the photoelectric current and the absorption become too small to measure. (The probability of the occurrence of a photoelectric effect diminishes as we go towards longer wave-lengths and this results in the fact that both the photoelectric current and the absorption become immeasurably small. It is just as true to say that the disappearance of the photoelectric effect is caused by the disappearance of the absorption as to say that the reverse is the case.) The fact that these experiments indicate the *separation* of an electron for each quantum absorbed implies that there is no place

[1] Z. Gyulai, *Zeits. f. Phys.*, **32**, 103 (1925).
[2] W. Flechsig, *Zeits. f. Phys.*, **46**, 788 (1928).

for a process corresponding to excitation (*e.g.*, as in gases) as an alternative to ionization.

Rocksalt, colored yellow through the presence of isolated sodium atoms dispersed throughout the lattice, gives a primary photoelectric current characteristic of many crystals which owe their origin to foreign particles. For the present we shall consider Gyulai's investigations on the photoelectric yield in so far as they bear on quantum equivalence.[1] The spectral distribution of the primary photoelectric current (referred to incident energy) and the spectral distribution of the absorption are given in Fig. 8-25. It will be seen that the two curves are nearly coincident, but that there is a discrepancy in the sense that the values for the photoelectric current become steadily greater, relative to the values for the absorption, as the wave-length increases. This is interpreted to mean that the yield increases in the same sense as the wave-length, which would be in accord with the view that the photoelectric effect is proportional to the number of quanta absorbed. Joffé[2] and Arsenjewa[3] maintain, on the contrary, that the photoelectric current is strictly proportional to the energy absorbed. Assuming that quantum equivalence is true for the primary electrons released, Arsenjewa suggests that secondary electrons are produced in greater numbers by the primary electrons released by the shorter wave-length. Experimentally, it is quite difficult to decide between the two views.

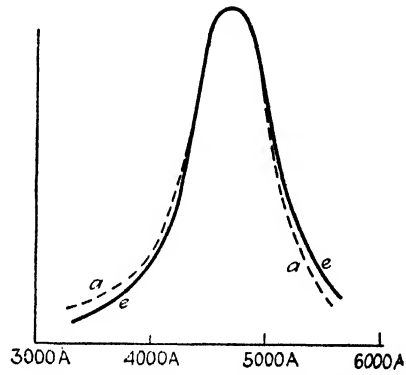

FIG. 8-25.—Spectral distribution in colored rocksalt. (*a*) Absorption. (*e*) Primary photoelectric current.

8-9. Instantaneity of the Primary Photoelectric Current.—Flechsig confirmed Gudden and Pohl's conclusion that the electron primary photoelectric current sets in at its full value the instant the light is turned on.[4] His method consisted briefly in applying an alternating field of "square" form to a crystal and measuring the current obtained as a result of flashing light on to it. The light could be flashed on to the crystal at any phase of the applied field. Its duration was 10^{-4} sec. The flow of electricity through the crystal as a result of this combination of flash and alternating field was carefully investigated. It was concluded that the electron primary photoelectric current began simultaneously with the illumination by blue light to within 10^{-4} sec, while the positive

[1] Z. GYULAI, *Zeits. f. Phys.*, **35**, 411 (1926).
[2] A. F. JOFFÉ, *loc. cit.*, p. 132.
[3] A. ARSENJEWA, *Zeits. f. Phys.*, **37**, 701 (1926).
[4] W. FLECHSIG, *Zeits. f. Phys.*, **33**, 372 (1928).

primary photoelectric current began simultaneously with infra-red illumination to within 10^{-1} sec. (The difference does not imply a lag in the

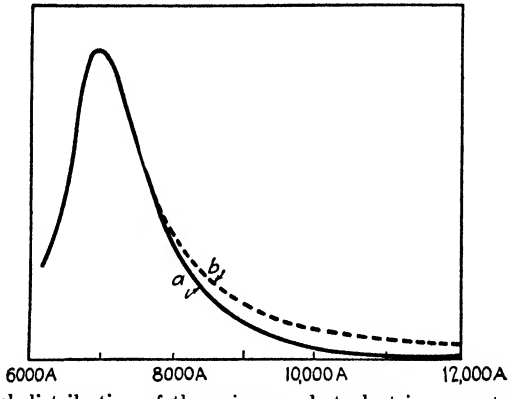

FIG. 8-26.—Spectral distribution of the primary photoelectric current in a red insulating selenium crystal. (*a*) In the unexcited state. (*b*) In the excited state.

latter case; it is merely that the experimental uncertainty is greater in this case.)

8-10. Crystal Excitation.—The spectral distribution of the electron primary current depends, in general, on whether or not the crystal has been recently illuminated. Thus Fig. 8-26 shows the distribution for a red insulating crystal of selenium, (*a*) after a strong illumination with long wave-length light (10,400A) to remove all positive charges, and (*b*) after short wave-length illumination (7500A) alone, as a result of which positive charges are left in the crystal.[1] When the crystal is in state *b* it is said to be "excited." No experimental curve for the optical absorption is available, but presumably it is *a* for the unexcited crystal and *b* for the excited crystal. However, there is no maximum in the absorption at about 7000A; the absorption gets larger and larger for shorter wave-lengths. The sudden drop in the photoelectric yield when the absorption attains a certain high value (coefficient ~ 0.1 mm^{-1}) is characteristic of diamond, zincblende, and selenium and, presumably, of all crystals in which the photoelectric effect is due to the material itself and not to foreign particles.

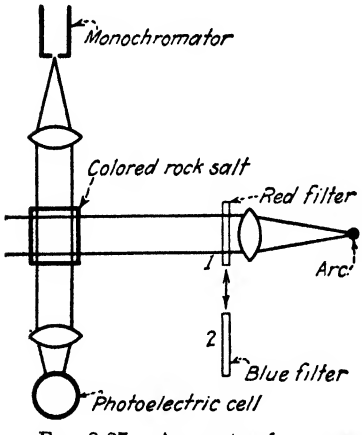

FIG. 8-27.—Apparatus for measuring absorption of excited and unexcited colored rocksalt.

[1] B. GUDDEN and R. POHL, *Zeits. f. Phys.*, **35**, 243 (1925).

Rocksalt, colored yellow by X-rays, is typical of crystals which owe their photoelectric properties to foreign atoms dispersed throughout the lattice. Gyulai used the arrangement shown in Fig. 8-27 for studying the absorption of colored rocksalt. The absorption coefficient was determined for monochromatic light by means of the photoelectric cell shown, (1) when the crystal was "excited" by flooding it with intense blue light from an arc lamp, and (2) when it was completely "unexcited"

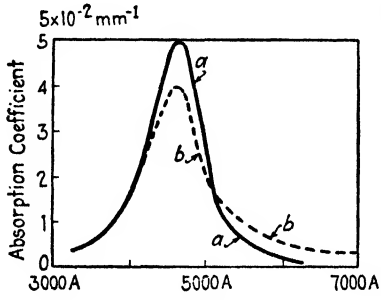

FIG. 8-28.

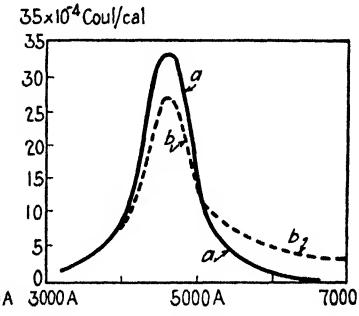

FIG. 8-29.

FIG. 8-28.—Absorption of colored rocksalt. (*a*) Unexcited crystal. (*b*) Excited crystal.
FIG. 8-29.—Primary photoelectric current in colored rocksalt. (*a*) Unexcited crystal. (*b*) Excited crystal.

by flooding it with intense red light. The results are given in Fig. 8-28. In Fig. 8-29 we have the spectral distribution of the photoelectric effect in the same rocksalt in the two states. The parallelism is so close that it may be confidently asserted that the new distribution in the photoelectric effect is closely associated with the (temporary) new distribution in the absorption coefficient. Absorption of light in the parts of the spectrum for which the crystal has a temporarily increased absorption causes a return to the unexcited state (*cf.* Sec. **8-23**).

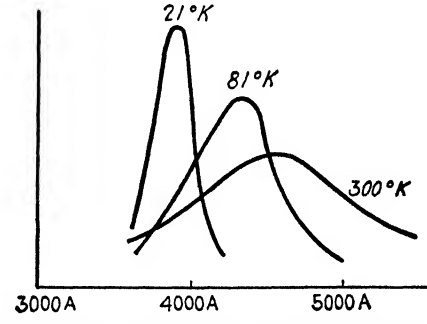

FIG. 8-30.—Primary photoelectric current in colored rocksalt: temperature effect.

Gudden and Pohl[1] found that the absorption curve of colored rocksalt in the unexcited state was shifted towards the violet and simultaneously narrowed by a decrease of temperature (Fig. 8-30). Although the curves become narrower at low temperatures, the total absorption apparently remains constant. The absorption spectra of a number of alkali halides, colored by X-rays, will be found in a paper by Ottmer.[2]

[1] B. GUDDEN and R. POHL, *Zeits. f. Phys.*, **34**, 249 (1925).
[2] R. OTTMER, *Zeits. f. Phys.*, **46**, 798 (1928).

Increase of temperature by itself produces a change in the optical absorption in the same sense as excitation, *i.e.*, a change from *a* towards *b* (Fig. 8-28), according to Flechsig.[1] Anything which contributes to a departure from perfection in the lattice flattens out the optical absorption curve and broadens it towards the long wave-lengths. Thus Flechsig has shown that colored synthetic rocksalt crystals have a broader curve than the more perfect (colored) natural rocksalt crystals. We are led to the view that a broadening of the optical absorption curves arises from anything which tends to make the lattice less perfect, whether this is due to permanent imperfections, or even to the departure of the atoms from their equilibrium positions as the temperature rises, or to excitation by short wave-length light in which the disturbance arises from the separation of electricity.

The maximum excitation which a crystal can endure depends on the temperature.[2] It is relatively large for colored rocksalt at low temperatures and diminishes at first slowly, then more rapidly to zero at about 10°C. The excess absorption due to excitation vanishes but slowly, especially at low temperatures.

8-11. The Positive Primary Photoelectric Current.—Gudden and Pohl consider that the electron primary photoelectric current is due to the separation of electrons from certain *centers* distributed throughout the crystal.[3] In crystals like rocksalt colored yellow by X-rays these centers are the foreign atoms distributed irregularly throughout the lattice, for pure rocksalt itself has no photoelectric effect. In crystals like diamond and zincblende in the purest and most perfect of which a strong photoelectric effect is found, Gudden and Pohl believe that only a relatively few "privileged" atoms are responsible for the photoelectric effect. The majority of atoms which fit normally into the regular crystal lattice are inactive, the atoms at the submicroscopic flaws, faults, or irregularities are those from which the photoelectrons are released and constitute the centers.[4] (In the sense that such

[1] W. Flechsig, *Zeits. f. Phys.*, **36**, 605 (1925).

[2] B. Gudden and R. Pohl, *Zeits. f. Phys.*, **31**, 651 (1925); Z. Gyulai, *Zeits. f. Phys.*, **39**, 636 (1926).

[3] B. Gudden and R. Pohl, *Zeits. f. Phys.*, **37**, 881 (1926). This paper contains the most recent formal account of Gudden and Pohl's theory.

[4] It is difficult to present positive evidence for the view that the normal atoms of the lattice are inactive photoelectrically. In support of this view, however, it might be argued that, if the normal atoms were the active "centers," there would be a definite strongly marked threshold corresponding to the electron affinity of the anion in the lattice. Also, in the case of the silver halides, it appears that the energy necessary to detach an electron from a halogen ion in the lattice is considerably larger than that corresponding to the wave-lengths of the radiation known to produce photoconductivity in these substances. (Unfortunately the constants do not appear to be known for zincblende, in which the primary photoelectric current has been studied very thoroughly.) The ions situated at the slight irregularities within the crystal probably

atoms are not orthodox members of the regular lattice, they may be regarded as distantly akin to the foreign atoms in rocksalt.) When a quantum of light is absorbed by a center it loses an electron and becomes positively charged. The electron moves towards the anode in an electric field, until it meets an obstacle which may be a foreign atom or a submicroscopic crack or discontinuity in the lattice. Even without an electric field it may possibly move a distance of several atomic diameters. With a sufficiently large field the electron can be driven through all such minor obstacles as may be found in a good crystal, and so a saturated electron primary photoelectric current may be obtained. The centers, however, do not remain positively charged. If they were all to become positive ions, their absorption spectra would be shifted a considerable distance into the ultra-violet. The fact that the position of the absorption spectrum is shifted but little suggests that the center becomes neutral by taking an electron from its surroundings. Thus it is now practically as it was before. Another quantum can now be absorbed and the process repeated with the result that the positive charge in the vicinity of the center increases. The broadening of the absorption curve towards longer wave-lengths is to be attributed to the fact that the neutral centers are now influenced by neighboring positive charges of varying intensities.

The positive charge in the space element adjacent to the center cannot build up beyond a certain value (which is higher the lower the temperature) without resulting instability. When it reaches the critical value, it is supposed that a rearrangement, perhaps a kind of local recrystallization, takes place, whereby the space element becomes once more neutral by capturing the necessary number of electrons from the space element adjacent to it on the side next the cathode. (In the absence of a field, the released electrons may be recaptured.) This process is repeated and so the location of the positive charge travels towards the cathode or is stopped by an obstacle. Warming the crystal promotes the mobility of the positive charge in that it allows instability to set in at lower excitation. Strong illumination by long wave-length light produces the same result and may perhaps, be regarded, as equivalent, in its effect, to a local heating of the excited space elements.

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lose electrons more readily than those located in the regular lattice. At different flaws, atoms with different amounts of electron affinity may be found; hence the absence of any definite threshold. Quite recently Zwicky (*Proc. Nat. Acad. Sci.* **15**, 816 [1929]) has maintained that there must be a secondary structure superposed on the fundamental lattice of any actual crystal. This secondary structure consists of blocks arranged with considerable regularity. The dimensions of these blocks lie between 100A and 10,000A. Within a block the lattice is ideal, but at the boundary of each block the continuity is broken. It may be that at such boundaries we have the location of the photoelectric effect.

Gudden and Pohl put forward a more specific theory of the action of long wave-length light in causing the shift of the positive charges accumulated in the neighborhood of a center.[1] They suppose that owing to the broadening of the absorption curve towards the longer wave-lengths, a temporary photoelectric effect by these longer wave-lengths becomes possible. Electrons are separated from the centers just as in the case of the short wave-lengths, until the excitation builds up to its critical value. Then the locations of positive charges slip back towards the cathode as described in the previous paragraph. The part played by infra-red light in quenching the excitation of a crystal is one of the most perplexing phenomena in this field. A study of the effect of infra-red light at low temperatures should throw some light on the problem.

Gyulai found that for every quantum of short wave-length light absorbed to produce the electron primary current, about one quantum of long wave-length light had to be absorbed to produce the corresponding positive primary current.[2] He also estimated that when the excitation reaches its maximum about 60 per cent of the centers are excited.

8-12. Initial Currents and Permanent Currents.—The success of Gudden and Pohl in disentangling the laws of the volume photoelectric effect in crystals is largely due to the simplicity gained by studying initial primary photoelectric currents for low light intensities and short times of illumination. We saw in Sec. **8-2**, how secondary currents which are not photoelectric in any sense can build up and eventually obliterate the primary photoelectric current. But even when conditions are such as to make these secondary currents negligible, there is much to be gained in the understanding of the primary photoelectric current itself by studying the *initial* values of these currents. We have seen that (*e.g.*, in a diamond), when a crystal is illuminated with blue light, the positive charges left behind when the photoelectrons are separated form an increasing positive space charge whose effect is in the direction of annulling the applied field. The effect of this is to diminish the measured current. On the other hand, when the excitation reaches its maximum possible value for the crystal and the working temperature, the positive charges will begin to move spontaneously towards the cathode so that the observed current will, from this cause, be larger than the initial electron primary current because it includes part of the positive primary current. These effects will modify the observed currents to an extent which depends greatly on the circumstances.

Gudden and Pohl found that the initial values of the electron primary current were quite independent of the temperature after allowance had been made for a slight change in absorption of light with

[1] B. Gudden and R. Pohl, *Zeits. f. Phys.*, **37**, 881 (1926). This paper contains the most recent formal account of Gudden and Pohl's theory.

[2] Z. Gyulai, *Zeits. f. Phys.*, **33**, 251 (1925).

the temperature.[1] This is as it should be for a simple photoelectric process. On the other hand, when permanent currents in illuminated crystals were studied by Lenz[2] as a function of the temperature, it was found that they were very much diminished at low temperatures, a change impossible to interpret photoelectrically (Fig. 8-31). However, the explanation is found in the fact that at low temperatures the excitation builds up to such a high value that the opposing field of the positive space charge almost annuls the effect of the applied field. This inter-

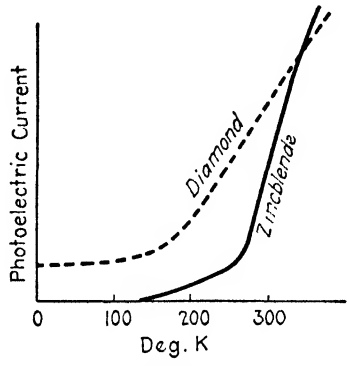


FIG. 8-31.—Permanent photoelectric current at different temperatures.

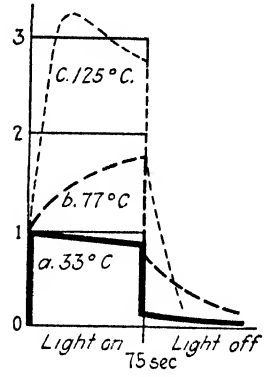


FIG. 8-32.—Photoelectric current in colored rocksalt at various temperatures due to blue light.

pretation is supported by Lenz's discovery that, when electrons (cathode rays) are shot into a crystal from outside, their motion inside is unaffected by low temperatures (down to liquid hydrogen). Here there is no space charge as there was in his photoelectric experiments.

Figure 8-32, which is reconstructed from Figs. 1, 3, and 5 of a paper by Gudden and Pohl,[3] is instructive in showing how the observed currents change with the time after the onset of illumination. The crystal used was rocksalt, colored yellow by X-rays. The way in which the current depends on the duration of illumination depends in a remarkable manner on the temperature of the crystal. At 33°C, only the electron primary current flows. It diminishes slightly with the time, owing to a growing polarization opposing the applied field.

When the photoelectrons and their corresponding positive charges are separated by but a short distance, as is implied when the currents are far below saturation, it is perhaps more in accordance with convention to speak of a polarization than of a positive space charge.

The slight current in the dark interval represents the almost negligible

[1] B. GUDDEN and R. POHL, *Zeits f. Phys.*, **34**, 249 (1925).
[2] H. LENZ, *Ann. d. Phys.*, **77**, 449 (1925).
[3] B. GUDDEN and R. POHL, *Zeits. f. Phys.*, **31**, 651 (1925).

spontaneous positive primary current. At 77°C, the current starts from the same initial value and approaches asymptotically to double the value. This is interpreted to mean that the excitation maximum of the crystal at this temperature is soon reached so that ultimately both the positive primary current and the electron primary current will flow together. (In the dark interval, there is a considerable flow of the positive primary current.) Finally, at 125°C, the current once more starts from its constant initial value but rapidly climbs to a value about three times as much. It will be remembered that the currents in rocksalt are far from saturation, which is accounted for by the hypothesis that the electrons travel but a short distance (0.0001 cm) before being stopped. Gudden and Pohl suggest that, at this high temperature, the heat motion of the lattice partly releases these trapped electrons. Hence the large observed current. These results again illustrate in a striking manner the various ways in which the current values change from their initial values when the temperature is changed.

8-13. Photoelectric Currents in Colored Rocksalt at Different Temperatures.—The complicated changes in the photoelectric currents resulting from changes of temperature and from changes in the amount of excitation are well illustrated in an investigation by Gudden and Pohl on colored rocksalt.[1] They show how necessary it is to use only initial currents obtained with low illumination if one wants to obtain any information about the fundamental photoelectric process underlying the various complicated results. The experiments were carried out at two levels of light intensity and three levels of temperature. In each case, the unexcited crystal was illuminated for a period of the order of a minute or two with blue light, then kept in the dark for about the same time and finally flooded with infra-red light. In Fig. 8-33*a* we have the simplest situation. We have the electron primary current alone; there is hardly any spontaneous positive primary current in the dark interval following. Illumination with infra-red light releases the positive primary currents, and the area under *mn* is about equal to that under *ce*. In Fig. 8-33*b* everything is as before except that the intensity of the light is much increased. The opposing field due to the large polarization now builds up rapidly and soon reduces the observed current to a fraction of its initial value. Figure 8-33*c* shows that at 77°C the spontaneous drift of the positive charges becomes more and more appreciable as the excitation rises, until the positive primary current is nearly equal to the electron primary current, thus making the final current nearly twice the initial current. The spontaneous drift of the positive charges continues through the dark interval *fjk*, and there is therefore less to be released during the infra-red illumination. In Fig. 8-33*d* we observe that the increasing

[1] B. Gudden and R. Pohl, *Zeits. f. Phys.*, **31**, 651 (1925).

polarization *de* soon offsets the spontaneous drift of the positive charge. The still higher temperature of 125° introduces more complications for, besides a strong spontaneous positive primary current, there is evidence that the high temperature begins to loosen the lattice in such a way as to allow the trapped electrons to move farther. It is important to notice the same inertialess change in the current when the blue light is turned

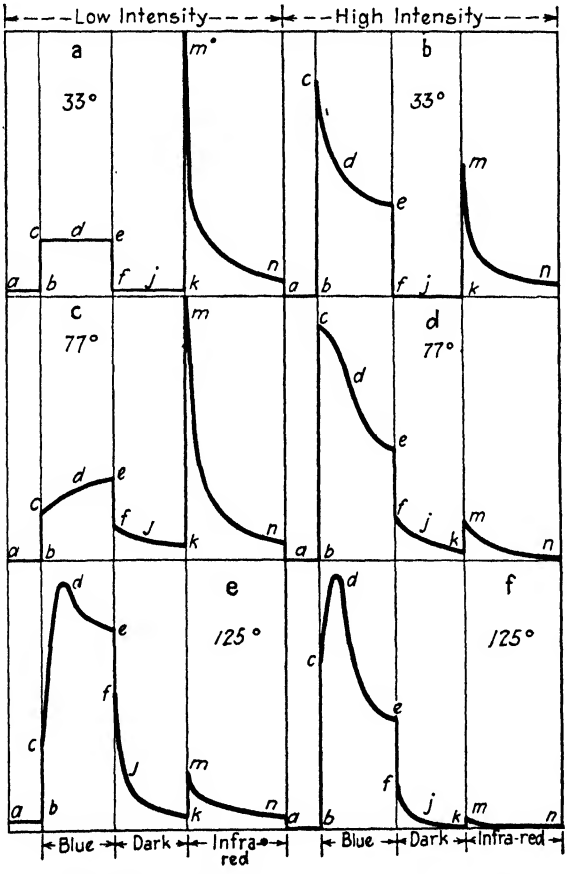


FIG. 8-33.—Photoconductivity in colored rocksalt.

on (*bc* in all the diagrams), and when it is turned off (*ef* in all the diagrams). This is evidence for the constancy of the fundamental electron primary current for constant light intensity.

8-14. Photoelectric Classification of Crystals.—Gudden and Pohl divide photoelectrically conducting crystals into two classes. To Class I belong the *idiochromatic* crystals whose photoelectric properties are determined by the material of the pure crystal itself and not by any naturally present, or artificially introduced, foreign matter. To Class II belong the *allochromatic* crystals; the crystals which are inactive photo-

electrically when pure, but which are active when certain foreign atoms or particles are dispersed throughout the crystal. This type of photoconductivity was discovered by Joffé in 1903, who noticed that exposure of rocksalt to X-rays or radium rays enabled it to conduct, when exposed to visible light, about a million times better than it did without such exposure.[1]

Typical examples of Class I crystals are diamond, zincblende, cinnabar, selenium (the red insulating crystal form), lead carbonate, and anthracene. It is a common property of all crystals in Class I that the optical refractive index in the region of the spectrum, far away from the absorption band, *i.e.*, in the region of high transparency, is very high. Pure crystals with refractive indices less than about 2, such as clear rocksalt, are inactive.

Class II crystals may be divided into two subdivisions. In Subdivision II*a*, we have crystals in which the foreign matter is distributed as colloidal particles, submicroscopic in size, but each particle consisting of many atoms, possibly forming minute crystals. Illustrations of such crystals are blue and speckled rocksalt (NaCl), sylvine (KCl), fluorite (CaF), and yellow citrine (SiO_2). The foreign matter may occur naturally or may be introduced artificially by electrolysis, or by long exposure to suitable metallic vapors. In Subdivision II*b*, we have crystals in which the foreign matter is probably distributed as isolated atoms in the crystal lattice (*e.g.*, yellow rocksalt).[2]

Each Class has its characteristic spectral distribution of photoelectric activity. In Class I crystals the photoelectric current is directly proportional to the number of quanta absorbed, and this increases as we go along the spectrum towards the ultra-violet. But when we get to the place where the absorption coefficient is increasing rapidly and passing through a value about 1 mm^{-1}, the photoelectric current suddenly falls off to zero (see Fig. 8-24). In crystals in which the foreign matter is distributed in atomic form (Subdivision II*b*), the photoelectric current follows closely with the optical absorption (Figs. 8-28 and 8-29). On the other hand, in crystals in which the foreign matter exists as colloidal particles, there is no close connection between the spectral distributions of the photoelectric current and the optical absorption as evidenced by Gyulai's results for blue rocksalt[3] (Fig. 8-34). The spectral distribution of the primary photoelectric current coincides roughly with that of the surface photoelectric effect for sodium metal. The inference is that the colloidal particles of sodium are big enough to emit electrons like sodium in bulk and not like single atoms. It is to be recorded that no excitation can be

[1] A. F. Joffé, *loc. cit.*, p. 127.

[2] Related properties of Class II*b* crystals are discussed in Sec. **8-23**.

[3] Z. Gyulai, *Zeits. f. Phys.*, **35**, 411 (1926).

found in blue rocksalt (Subdivision II*a*),[1] although when the color is due to foreign atoms (Subdivision II*b*) excitation can be produced as we have already seen.

In certain Class I crystals, a saturated primary photoelectric current can be obtained (at any rate for flawless crystals) with fields of the order of 15,000 volts/cm, and for thicknesses of about 1 mm. Gudden and Pohl observed that, in general, the higher the refractive index in the highly transparent region, the lower the voltage necessary to saturate the current.[1] No satisfactory explanation is forthcoming. Kurrelmeyer could find no evidence at all for approaching saturation in apparently good crystals of sulphur.[2] Perhaps there is some significance, in view of Gudden and Pohl's results, in the fact that the optical refractivity

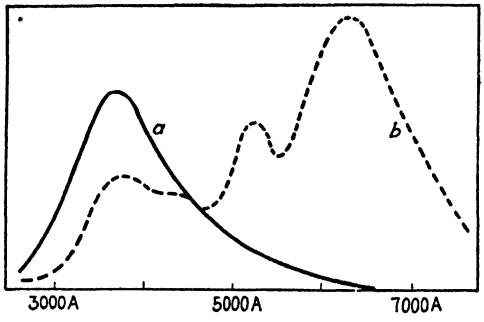


FIG. 8-34.—Spectral distribution in blue rocksalt. (*a*) Primary photoelectric current. (*b*) Absorption coefficient.

of sulphur is close to 2, which is almost the lowest value a Class I crystal can have and still exhibit a photoelectric effect. In Class II crystals it appeared for a long time that the primary photoelectric current obeyed Ohm's law, thus showing no indication of approaching saturation, even in a field of 80,000 volts/cm. That the difference is one of degree rather than of kind follows from Flechsig's work[3] in which he showed that, in very thin crystals (about 0.1 mm thick), saturation can be obtained in fields of about 40,000 volts/cm.[4] In Sec. **8-1** the distance x, moved through by an electron in an electric field F, is assumed to be given by $x = kF$. k is thus a measure of the ease of driving an electron through the lattice, and in fact is the distance through which an electron would be driven by unit force. From Eq. (8-8), we have $k = d^2/V_s = d/F_s$, where the subscript refers to saturation values. For diamond or zinc-

[1] B. GUDDEN and R. POHL, *Zeits. f. Phys.*, **23**, 417 (1922).

[2] B. KURRELMEYER, *Phys. Rev.*, **30**, 901 (1927).

[3] W. FLECHSIG, *Zeits. f. Phys.*, **46**, 788 (1928).

[4] Diminishing the thickness of the crystal is advantageous not only because it enables a higher field to be obtained with a given potential, but because, in addition, the electrons have less distance to travel.

blende, k is of the order (0.1/15,000) cm²/volt = 61×10^{-7}; while for Flechsig's rocksalt, k is of the order (0.01/40,000) cm²/volt = 2.5×10^{-7}. Thus, under the same field, an electron will travel 61/2.5 = 25 times as far in the first crystals as in the colored rocksalt. It has been assumed that in a perfect lattice the electrons would move through it unhindered. In real lattices they are brought to a stop by some "obstacle" which in a Class I crystal may be a submicroscopic crack or defect, while in a Class II crystal it may be these or one of the foreign atoms. On this assumption there should be 25^3 or about 15,000 times as many effective obstacles per unit volume in Flechsig's colored rocksalt as in the best diamond.

8-15. Photoelectric Conduction in a Magnetic Field.—In 1916, Lukirsky[1] found a Hall effect in photoelectrically conducting crystals, which indicated that electrons were the carriers of the current. (No measurable Hall effect is to be expected for electrolytically conducting substances.) Lenz[2] made a systematic investigation of the Hall effect in diamond and in zincblende (using electrons driven in by bombardment by cathode rays, as well as photoelectric currents). A suitable crystal, mounted between electrodes (Fig. 8-35), was placed in a magnetic field whose axis is perpendicular to the plane of the paper. Two electrodes A and B, connected to a suitable electrometer, measured the Hall e.m.f., set up as a result of the magnetic field. For diamond the results are summarized in Fig. 8-36. To compare these results with theory, we give the following condensed account of Lenz's presentation. Let E_x be the applied electric field driving the current along the x-axis, and E_y the field parallel to the y-axis which is built up to prevent the flow of electrons parallel to the y-axis, when the magnetic field H is applied. If e and m be the charge and mass of the electron, then the equations governing the motion are

$$\begin{aligned} m\ddot{x} &= eH\dot{y} + eE_x, \\ m\ddot{y} &= -eH\dot{x} + eE_y. \end{aligned} \tag{8-10}$$

On making suitable approximations, it is found that these equations lead to the result that if an electron moves freely under the forces contemplated in Eqs. (8-10) for a time t, then

$$\frac{E_y}{E_x} = \frac{1}{3}\frac{e}{m}Ht. \tag{8-11}$$

The distance x' moved through by an electron is given by

$$x' = \frac{1}{2}E_x\frac{e}{m}t^2. \tag{8-12}$$

Thus x' is to be regarded as a free path through which an electron can

[1] Quoted by A. Arsenjewa, *Zeits. f. Phys.*, **37**, 701 (1926).

[2] H. Lenz, *Phys. Zeits.*, **25**, 435 (1924); *Ann. d. Phys.*, **77**, 449 (1925); **82**, 775 (1927).

move freely before a collision of some sort abruptly violates the conditions under which Eqs. (8-10) are applicable. Equations (8-11) and (8-12) yield

$$E_y = H(x'E_x)^{\frac{1}{2}}\left(\frac{2e}{9m}\right)^{\frac{1}{2}}. \tag{8-13}$$

This asserts that the Hall e.m.f. should be proportional to the magnetic field, which is experimentally the case (Fig. 8-36*a*). Figure 8-36*b*

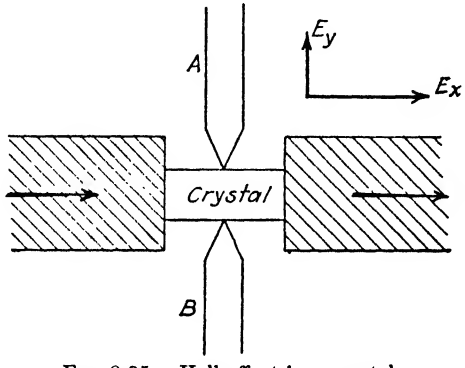


FIG. 8-35.—Hall effect in a crystal.

shows that the Hall e.m.f. is directly proportional to the applied field up to 4000 volts/cm. This implies that x' in Eq. (8-13) should be proportional to E_x. This is reasonable enough and is in accord with the view given in Sec. **8-1** of the current-potential relations in crystals. However, there the distance x was the distance traversed by the electron before it

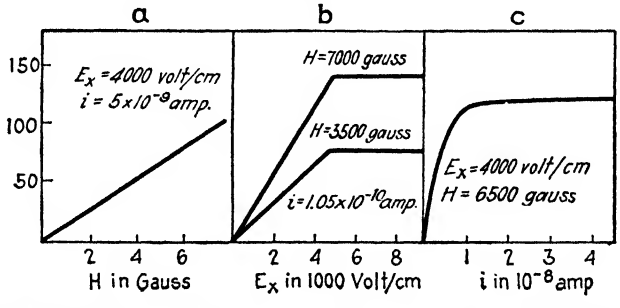


FIG. 8-36.—Hall effect in a diamond (6.4 × 4.0 × 1.3 mm). Ordinates, in each case measure the Hall e.m.f. in volts/cm.

met an obstacle at which it was stopped and held fast. Thus the x of Sec. **8-1** may be far larger than this x'. Using his experimental data for a field of 4000 volts/cm and a magnetic field of 4000 gauss, Lenz computed the free path x' to be 3.4×10^{-6} cm. As the potential used by Lenz is almost certainly greater than say one-tenth of the saturation potential, Eq. (8-5) indicates that x must be of the order 10^{-2} cm. No

explanation was offered by Lenz for the flattening out of the curves in Fig. 8-32*b* at 4000 volts/cm. It may possibly have to do with the attainment of saturation in the crystal. Unfortunately Lenz does not record the saturation field for his diamond, but 4000 volts/cm, though smaller than the saturation field recorded by Gudden and Pohl for their diamond, is nevertheless of the same order of magnitude.

The results were less conclusive for zincblende, although with some crystals, in certain orientations, the Hall effect indicated that the electrons were the carriers of the current. Lenz attributed the anomalous behavior to inhomogeneities and possibly to certain orientations of the axes of the crystal. These are problems more intimately related to the conducting properties of crystals than to the photoelectric effect itself.

Since the Hall effect was of the same order of magnitude at liquid-air temperatures as at room temperatures, Lenz concluded that free-path phenomena are not altered by change of temperature. This is supported by the fact that temperature has no effect on the conductivity of a crystal for electrons driven into it by cathode-ray bombardment, nor has it on the *initial* primary photoelectric current.

Tartakowsky[1] mounted a crystal between two electrodes, the anode being split into two parts, between which the current was shared equally. The superposition of a magnetic field at right angles to the electric field resulted in a greater number of electrons arriving at one half of the anode than at the other, owing to the deviation of the paths of the electrons. On removing the magnetic field, the half, which in its presence received most of the electrons, now received the least. This was interpreted to indicate that the effective field is diminished by an amount which increases with the magnitude of the electron space charge built up in front of the anode. We thus have evidence that negative space charges can be built up in crystals as well as positive space charges.

8-16. Secondary Currents.—The way in which secondary currents arise from, and are superposed on, the primary photoelectric current was discussed very briefly in Sec. **8-2.** According to the experimental results plotted in Figs. 8-8 and 8-10, the quantity of electricity registered by the instrument in series with the illuminated crystal can be expressed as a parabolic function of t, the duration of the illumination,

$$Q = At + Bt^2.$$

In terms of currents, we have

$$\frac{Q}{t} = I_p + I_s,$$

where I_p is the primary photoelectric current which is independent of the time t, and I_s ($= Bt$) is the secondary current, which is, initially at least, directly proportional to the duration of the illumination. I_p depends on the applied potential in the way shown in Fig. 8-9, and is directly

[1] P. Tartakowsky, *Zeits. f. Phys.*, **66**, 830 (1930).

proportional to the intensity of radiation (Fig. 8-10). We may therefore write $I_p = \alpha \cdot S \cdot f(V)$, where S is the light intensity, and $f(V)$ is a function of the applied potential. Similarly we may write $I_s = kt \cdot \beta S^2 \cdot F(V)$, which expresses the result that I_s increases proportionally to the duration of the illumination, that it depends on the potential according to the lower curve in Fig. 8-8, and that it increases (but only approximately) as the square of the light intensity (Fig. 8-10). Thus I_p has all the characteristics which we should expect for a current of electrons released photoelectrically. I_s, on the other hand, is more indefinite. Gudden and Pohl[1] regard the passage of the primary photoelectric current as disturbing the lattice in such a way that the small conductivity which the lattice has in the dark is increased very considerably. Hence the secondary current I_s, dissected out from the curves in Fig. 8-7, is a large-scale reproduction of the current which flows in the dark (Fig. 8-6). Since I_s depends on a disturbance built up cumulatively as a result of the passage of the primary current, we should expect it to increase with the time, as indeed it does. (This increase no longer holds, however, when the excitation reaches its limiting value at which it breaks down spontaneously.)

The extensive investigations of Tubandt and of Joffé on currents through ionic crystals (unilluminated) led them to conclude that the conductivity was electrolytic in nature. On the basis of the striking resemblance between the current-potential relation for zincblende in the dark, and for the secondary current through it when illuminated, Gudden and Pohl concluded that the secondary current was also electrolytic. In agreement with this view is the fact that a crystal is sometimes permanently altered and, in particular, its conductivity permanently increased, by intense illumination in a field. The formation of invisible fibers (perhaps metallic) forming bridges between the electrodes may be the cause. Some alternative explanation appears to be necessary for diamond and other non-ionic crystals. Kurrelmeyer was unable to find any secondary current in sulphur.[2]

According to Hevesy[3] and Smekal,[4] the passage of an electrolytic current through an ionic crystal is facilitated by the presence of microcrystalline surfaces. Apparently anything in the nature of a flaw, forming a surface of discontinuity within the crystal, is a region along which ions can pass readily. Thus in imperfect crystals and in compressed powders, very large secondary currents may be obtained. We have seen that departures from perfect regularity in a crystal diminish the primary photoelectric current. Hence, as we pass from perfect crystals to imper-

[1] B. Gudden and R. Pohl, *Zeits. f. Phys.*, **6**, 248 (1921).
[2] B. Kurrelmeyer, *Phys. Rev.*, **30**, 901 (1927).
[3] See A. F. Joffé, *loc. cit.*, p. 97; also *Zeits. f. Phys.*, **62**, 730 (1930).
[4] A. Smekal, *Zeits. f. Phys.*, **55**, 289 (1929).

fect crystals, the ratio of the secondary currents to the primary photoelectric currents increases tremendously, with the result that in many cases the secondary current may completely obscure the primary photoelectric currents.

According to Joffé,[1] the heat of dissociation in the surface layers of a crystal is about half the value for the interior. Hence a compressed powder, because of the large total effective surfaces, has a much higher conductivity than a single crystal. It should be recorded that, because of the uniformity in the conductivity of carefully prepared pure crystals, Joffé does not agree with Hevesy's view that the small conductivity in single perfect crystals is to be ascribed to irregularities in the lattice spaced by distances of the order of 10^{-6} cm. However, Zwicky[2] has brought forward strong evidence for the view that in all actual crystals there is a secondary structure possessing a considerable regularity necessarily superposed on the lattice structures.

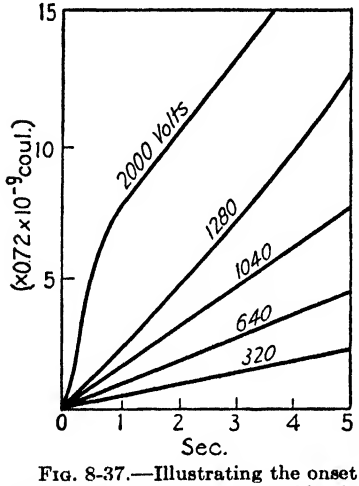


FIG. 8-37.—Illustrating the onset of a secondary current. Zincblende (1 cm² × 1 mm). λ = 3130A. Light intensity 12.5 × 10^{-7} cal/sec cm².

A current similar to the secondary current can be obtained merely by diminishing the resistance through increase of temperature. It is therefore obvious why the secondary currents through a crystal increase rapidly with the temperature. (It will be remembered that the primary photoelectric current was independent of the temperature.) In accord with this, it is found that experiments on the primary photoelectric current are not interfered with by secondary currents nearly as much at low temperatures as at high temperatures.

One fact alone which rules out the interpretation of a secondary current as a photoelectric effect is that the currents obtained (*e.g.*, in a selenium cell) are so large that they imply the release of many electrons for each quantum absorbed—a result directly at variance with the fundamental hypothesis that one quantum can release only one electron. (There is a striking parallelism here with cases frequently met with in physical chemistry, in which the absorption of one quantum results, not in the dissociation of a single molecule, but in the dissociation of hundreds or thousands. Here a chain of reactions is initiated by the molecule absorbing the quantum.)

[1] A. F. JOFFÉ, *loc. cit.*, p. 97; *Zeits. f. Phys.*, **62**, 730 (1930).
[2] F. ZWICKY, *Proc. Nat. Acad. Sci.*, **15**, 816 (1929).

The growth of the secondary current for weakly absorbed radiations is shown in Fig. 8-7. For very strongly absorbed radiations, the corresponding effect is illustrated in Fig. 8-37. Here the secondary current increases at first rapidly (as in Fig. 8-7) but ultimately settles down to a steady value. The 2000-volt curve in Fig. 8-7 can be made to resemble that in Fig. 8-37 merely by increasing the intensity of the light. Hence the difference between the two cases depends only on the amount of light absorbed per unit volume, and not on the difference in absorption coefficients. Figure 8-37 shows that the contribution of the secondary current to the total quantity of electricity transferred settles down to a steady value after the first two seconds or so. Evidently the change in the

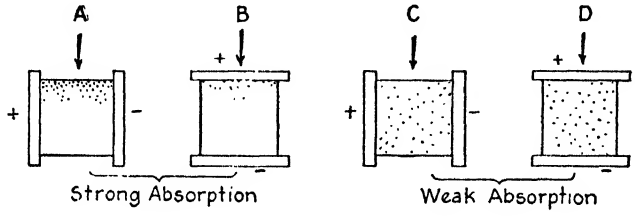


FIG. 8-38.

resistance of the lattice reaches a constant value after a finite time, which is shorter the more intense the illumination.

Gudden and Pohl have pointed out that the largest secondary currents are to be found when the current density of the primary photoelectric current is greatest. The latter current is determined merely by the total number of quanta absorbed and it is immaterial whether the crystal is illuminated transversely or longitudinally. The secondary current, on the other hand, is much stronger in case A (Fig. 8-38) than in any other, for here there is a thin layer all along which a large diminution in resistance is produced by the primary photoelectric current.

It will be remembered that the primary photoelectric current diminished rather abruptly to zero when the absorption coefficient increased beyond a certain critical value. Why this was so could not be explained, but it seems clear that the disturbance of the lattice produced by light still exists in the thin layer in which it is absorbed, and hence the secondary current can be traced farther towards the ultra-violet than the primary photoelectric current. This is illustrated in Fig. 8-39 which reveals the rise in the secondary current as the applied potential is increased and the simultaneous shift of the maximum towards the violet. The crystal used was cinnabar, which becomes opaque beyond about 6000A, hence the falling off of the primary photoelectric current at about 6200A (*cf.* diamond at about 2500A).

In contrast with the behavior of the primary photoelectric current, which establishes itself instantaneously, the secondary current takes time

to build up (Figs. 8-7 and 8-37) and continues for some time after the illumination is cut off. An extreme example of this appears in Fig. 8-40. Moreover, it shows dependence on past treatment (Fig. 8-41). Gudden points out that the method of representation here tells us nothing about the way in

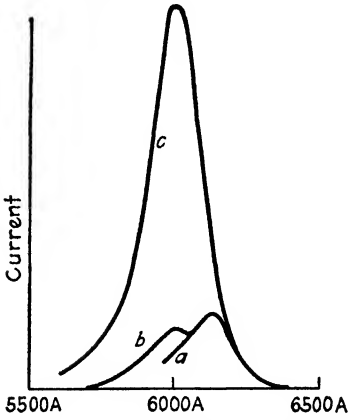


FIG. 8-39.—Development of secondary current with increasing voltage in cinnabar (HgS): (*a*) 100 volts, primary current only; (*b*) 200 volts, first appearance of secondary current; (*c*) 700 volts, secondary current predominates.

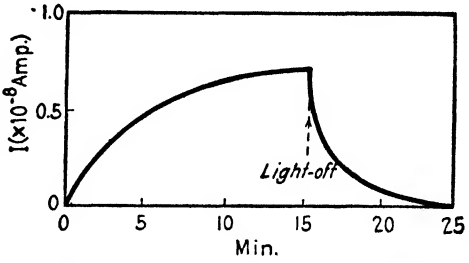


FIG. 8-40.—Time lag in greenockite (CdS). λ = 6800A (weakly absorbed).

which the secondary current is built up on the primary. If the progress of the curve *a* (Fig. 8-41) had been studied step by step within the first second or so, no doubt the growth of the secondary current on top of

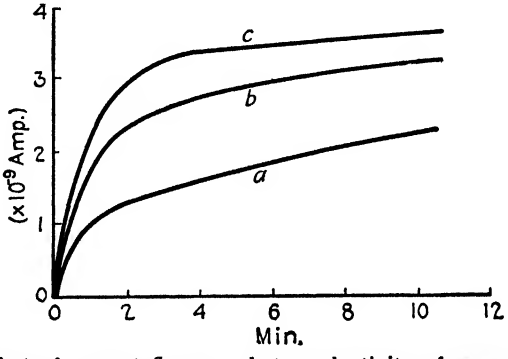


FIG. 8-41.—Effect of current flow on photoconductivity of greenockite (CdS). (*a*) First experiment. (*b*) Second experiment. (*c*) Third experiment. (The experiments followed each other immediately.)

the instantaneously established primary photoelectric current could be traced out much as in Figs. 8-7 and 8-37.

Runge and Sewig[1] attempted to account for the secondary current quantitatively. They assumed that the primary photoelectric current produced a certain number, p, of disturbances in the lattice per second. The number of these disappearing spontane-

[1] I. RUNGE and R. SEWIG, *Zeits. f. Phys.*, **62**, 726 (1930).

ously was assumed to be proportional to the number present at any given time. Hence the rate of formation of these disturbances is given by

$$\frac{dy}{dt} = p - ky,$$

the solution of which is

$$y = \frac{p}{k}(1 - e^{-kt}).$$

If the current due to illumination is proportional to y and the current in the dark is i_0, then the current at any time t should be

$$i = i_0 + i_1(1 - e^{-kt}),$$

where i_1 is the current due to the light when the exponential term is negligible. An oscillograph study of the current through a certain type of thalofide cell showed that this equation was adequate to describe the results. Since k was $\sim$470 sec^{-1}, current fluctuations of a period of 0.01 sec or more could be recorded without appreciable distortion.

PHOTOCONDUCTIVITY IN PARTIAL CONDUCTORS. BEARING OF PHOTOCONDUCTIVITY IN OTHER FIELDS

Many substances are now known to show a change in conductivity when illuminated. When the conductivity due to illumination can be interpreted directly in terms of the motion of electrons released individually by the absorption of quanta of radiation, the process has been termed photoelectric conduction. But in many substances no such simple interpretation can be made. We merely know that light produces a change in conductivity, the conditions, however, allowing all sorts of superposed secondary effects to mask, more or less completely, the fundamental photoelectric effect which is no doubt the direct result of the absorption of radiation. The photoconductivity of selenium has been investigated many times, but only in one investigation, that by Gudden and Pohl, when the selenium was studied as a single insulating crystal, has it been possible to demonstrate that the conductivity has the characteristics to be expected of a photoelectric effect. It is only for a very special class of substances—large, single, highly insulating crystals—that it is possible to show directly that the photoconductivity observed is fundamentally a photoelectric process. Gudden and Pohl were also able to trace the beginning of the secondary effects, which even in these single insulating crystals may easily grow to such a value as to obscure the direct photoelectric process. The secondary effects had many of the characteristics of the photoconductivity exhibited by substances which are neither single crystals nor good insulators, and so it is a natural inference that what is observed in the majority of photoconducting substances is merely the superposition of large secondary effects upon a basic photoelectric effect.

Between 1900 and 1917, stibnite (Sb_2S_3), cuprous oxide (Cu_2O), some salts of silver, iodine, and mercuric chloride (HgI_2) were added

to the list of photoconducting substances hitherto represented by selenium alone. In 1917, Case[1] examined about 170 substances, nearly all minerals, for photoconductivity and found 19 to possess this property in some degree. These were selenium, stibnite (Sb_2S_3), bismuthinite (Bi_2S_3), molybdenite (MoS_2), argentite (Ag_2S), galenite (PbS), acanthite (Ag_2S), pearcite (Ag_9AsS_6), miargyrite ($AgSbS_2$), jamesonite ($Pb_2Sb_2S_5$), bournonite ($3[Cu_2,Pb]SSb_2S_3$), boulangerite ($Pb_3Sb_2S_6$), pyrargyrite (Ag_3SbS_3), proustite (Ag_3AsS_3), stephanite (Ag_5SbS_4), polybasite (Ag_9SbS_6), iodyrite (AgI), cuprite (Cu_2O), and silver oxide (Ag_2O) tablets. Other substances have been added to the list by subsequent workers. All these substances, which are imperfect crystals or many small crystals welded together, show some slight conductivity in the dark.

To recapitulate the difference between a pure photoelectric current and one on which a typical secondary current is superposed, we tabulate the characteristics as follows:

Primary Photoelectric Current	Secondary Current
Follows changes in illumination instantaneously.	Time lag.
Current directly proportional to light intensity.	Absence of proportionality; frequently hysteresis effect.
Saturation currents independent of field obtainable with sufficiently high fields.	Currents not a simple function of the field.
Independent of temperature.	Strongly dependent on temperature; form of dependence far from simple.
Quantum equivalence.	Quantum equivalence frequently much exceeded.
Best studied in perfect crystals.	Larger, the more imperfect the crystal.

Excepting the single crystals examined by Gudden and Pohl, the conductivity of photoconducting substances has the characteristics enumerated in the second column. It is impossible to separate the superposed secondary currents from the fundamental photoelectric process. Consequently the results of the investigations on these photoconducting substances are useless in shedding any light on the fundamental photoelectric process, beyond merely indicating its presence. However, so many investigations have been made that it is desirable to record the typical results very briefly, and to emphasize that they have only an empirical value.

8-17. Sulphides.—Coblentz[2] investigated the photoconductivity of many mineral sulphides and devoted special attention to the properties of molybdenite (MoS_2). The specimen was mounted in series with a galvanometer and a battery. As the specimens usually had a conductivity in the dark, it was found convenient to limit the applied potential

[1] T. W. Case, *Phys. Rev.*, **9**, 305 (1917).

[2] W. W. Coblentz and H. Kahler, *U. S. Bur. Standards, Bull.* **15**, 121 (1919).

to about 3 volts at room temperatures and to about 100 volts at liquid-air temperatures.

The *spectral distribution* of the photoconductivity of molybdenite was obtained for an "equal energy spectrum." (This was accomplished

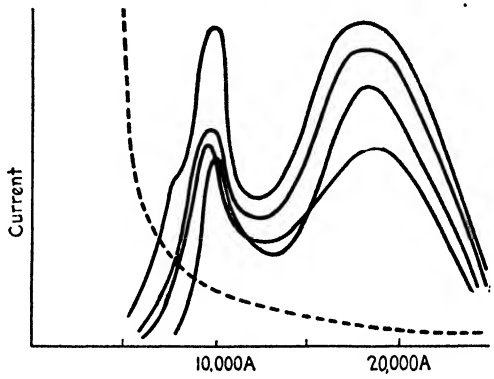


FIG. 8-42.—Photoconductivity in molybdenite at 22°C (two crystals, illuminated at different spots). Broken line, absorption curve. Illumination time presumably "unlimited."

by arranging that the narrow band, separated by the monochromatic illuminator, produced equal effects on a thermopile.) A typical spectral distribution curve is shown in Fig. 8-42. The molybdenite was insensitive in the infra-red beyond 25,000A. The diagram indicates perhaps a greater amount of reproducibility than an examination of the many curves obtained by Coblentz and Kahler indicates. The relative heights of the principal maxima change greatly from one specimen to another, although their positions remain fairly stationary. In thicknesses of 0.007 mm the molybdenite has a deep-red color in accordance with the absorption coefficient plotted in the diagram.

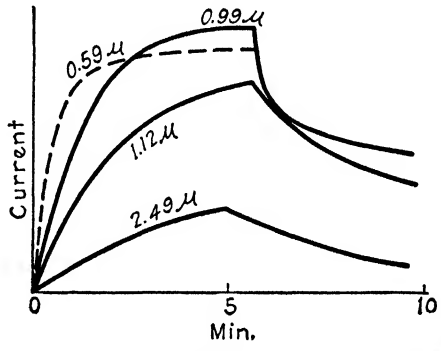


FIG. 8-43.—Change of photocurrents in molybdenite with time before and after cutting off the light. Wave-length of light used indicated on each curve. (Broken line not in the original drawing: inserted from data in the original article.)

While it is tempting to associate the shorter wave-length maximum with the rapid change in the absorption coefficient, in accord with the results found by Gudden and Pohl for the primary photoelectric current and the superposed secondary current (Sec. **8-16**), the presence of the 18,000A maximum cannot be correlated with any change in the absorption coefficient. The effect of *duration of illumination* is shown in Fig. 8-43. The shorter the wave-length, the more rapid is the response. Similar

results were obtained at liquid-air temperatures. The difference in lag is shown in a striking manner in Fig. 8-44. By "unlimited" exposure is meant that exposure, possibly amounting to several minutes, which is necessary to allow the current to reach a sensibly

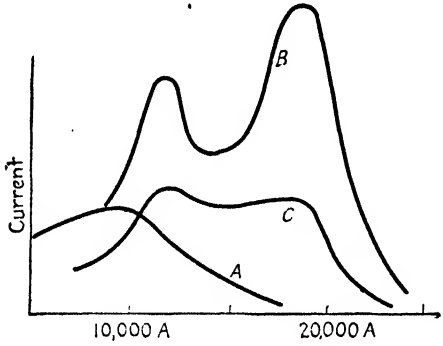


FIG. 8-44.—Photocurrents in molybdenite. *A*. Ten seconds exposure; light intensity = 20. *B*. "Unlimited" exposure; light intensity = 20. *C*. "Unlimited" exposure; light intensity = 1.

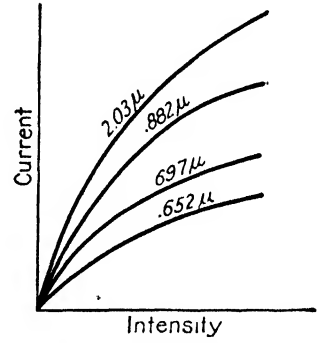


FIG. 8-45.—Dependence of a current through molybdenite on the intensity of illumination.

constant value. The effect of *intensity of illumination* is also shown in Fig. 8-44, as well as in Fig. 8-45. For unlimited exposures, the current curves may be represented by $I \propto E^{0.4}$, where E is the intensity of the light. The effect of lowering the *temperature* to that of liquid air is to increase very greatly the small maximum at 8500A. The

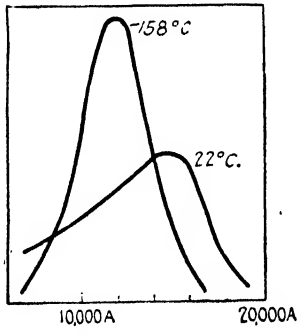


FIG. 8-46.—Photocurrents in acanthite (Ag_2S).

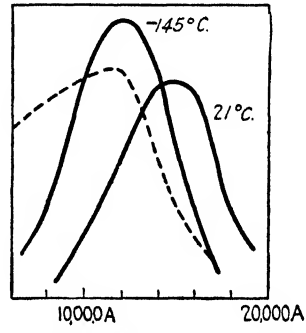


FIG. 8-47.—Photocurrents in argentite (Ag_2S). (Broken line for artificial Ag_2S.)

other maxima (at 10,000A and 18,000A) are in some cases increased, in others they disappear. The effect of *electric field* was not investigated. Applied voltages of about 2 to 4 volts were used in room-temperature experiments. At liquid-air temperatures, 40 to 100 volts were used. The reason for this is that Coblentz and Kahler were interested in comparing the conductivity due to light with the natural conductivity in the

dark. Thus it is not evident what would happen on changing the temperature without changing the voltage. For artificial MoS_2, pressed into tablets, only one maximum at 8000A appeared.

Mineral silver sulphide (Ag_2S) shows photoconductivity in two forms, argentite and acanthite. The spectral distributions are shown in Figs. 8-46 and 8-47. Figure 8-47 shows the same thing for artificially prepared Ag_2S. When it is remembered that the curves obtained for different specimens of these minerals vary considerably among themselves, we may omit the slight differences between the two upper left-hand curves and conclude that the maxima come at sensibly the same place and are shifted towards the violet by about the same amount by lowering of temperature. The curves for the minerals differ appreciably from those for the artificial substances.[1] The spectral distribution for stibnite (Sb_2S_3) was investigated by Elliott[2] and the results shown in Fig. 8-48. The currents (for presumably "unlimited" exposure) were found to be proportional to the square root of the intensity of the light.

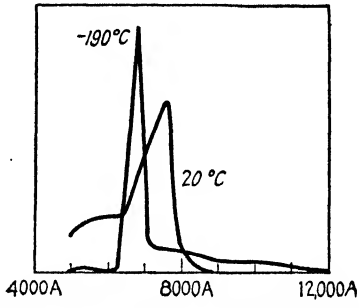


FIG. 8-48.—Photocurrents in stibnite (Sb_2S_3).

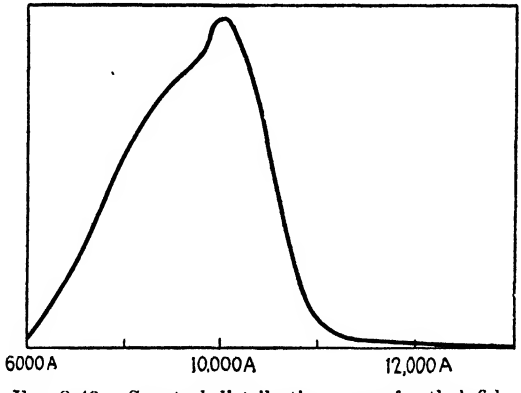


FIG. 8-49.—Spectral distribution curve for thalofide.

In the case of proustite (Ag_3AsS_3), lowering the temperature, step by step, gradually suppresses the maximum at 4600A, and brings out more and more intensely the maximum at 5800A. Bournonite [$3(Cu_2,Pb)SSb_2S_3$] and

[1] As long ago as 1885, S. Bidwell (*Phil. Mag.*, **20**, 178 [1885]) had shown that the conductivity of a thin layer of silver sulphide was increased by exposure to burning magnesium ribbon. E. Mercadier and G. Chaperon (*Jour. d. Physique*, **9**, 336 [1890]) showed that this extended from the ultra-violet to the infra-red in qualitative agreement with the results of Coblentz.

[2] D. S. ELLIOTT, *Phys. Rev.*, **5**, 53 (1915).

pyrargyrite (Ag_3SbS_3) were investigated by Coblentz and Eckford,[1] for comparison with the simpler sulphides of which they are composed, *viz.*, Ag_2S and Sb_2S_3 (which are photoconducting), and CuS and PbS (which are not). Their spectral distribution curves do not resemble those for the simpler sulphides.

8-18. Thalofide.—With a view to securing an improvement on the selenium cell, Case developed a preparation compounded of thallium, oxygen and sulphur, to which he gave the name of "thalofide" and which shows considerable photoconductivity.[2] The substance is mounted on a small quartz disk and kept in a vacuum and in a red bulb as the blue end of the spectrum deteriorates it. To give a rough idea of the order of the

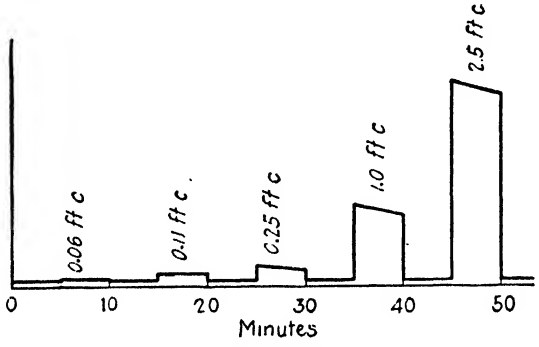


FIG. 8-50.—Speed of response in a thalofide cell (ft c = foot candles).

characteristics of the usual thalofide cell, we may state that the dark resistance generally lies between 5 and 500 megohms, and that light of intensity 0.25 footcandle diminishes the resistance to about one-half. The spectral distribution is shown in Fig. 8-49. The sensitivity drops abruptly from the maximum at 10,000A to zero at 12,000A. The quickness of response is shown in Fig. 8-50. Here the cell is alternately illuminated and kept in the dark for periods of 5 min each. The intensity of the illumination in the successive illuminations is shown in the diagram. The response shown here is very quick compared with that of the other photoconducting sulphides and of most selenium cells. On the other hand, Coblentz found that the conductivity continues to increase appreciably for at least two minutes after the light is turned on.[3] Kaplan observed that, while with small radiation intensities the final value of the conductivity of thalofide was reached in a few seconds, it took several minutes to reach the final value with large intensities.[4] He noted that the final value was always the same for the same intensity of radiation. Kaplan points out that a thalofide cell is about sixty times as sensitive an

[1] W. W. COBLENTZ and J. F. ECKFORD, *U. S. Bur. Standards, Bull.* **18**, 353 (1922).
[2] T. W. CASE, *Phys. Rev.*, **15**, 290 (1917).
[3] W. W. COBLENTZ, *U. S. Bur. Standards, Bull.* **16**, 254 (1920).
[4] J. KAPLAN, *Jour. Opt. Soc. Amer.*, **14**, 253 (1927).

indicator in infra-red spectroscopy (*i.e.*, between 8000A and 11,000A) as a Hilger thermopile. Improvements in the technique of preparing the compound have made it possible to prepare cells having the same sensitivity as Case's thalofide cells with only one-fiftieth of their resistance.[1]

8-19. Photonegative Effects.—In several investigations it has been found that some photoconducting substances show under certain circumstances a diminution in conductivity on illumination (selenium, Ries[2] and Brown;[3] stibnite, Elliott;[4] molybdenite and acanthite, Coblentz[5]). The results are very difficult to correlate and it seems best to select a few typical illustrations from the work of Coblentz. The specimen was mounted in series with a galvanometer; zero galvanometer deflection means the reading of the galvanometer when the steady dark current has been obtained. The effect of light is usually to increase the conductivity (the photopositive effect, above the zero axis), but occasionally it is found that light apparently diminishes the conductivity (the photonegative effect, below the zero axis). The photonegative effect occurs above a critical voltage whose value depends on the temperature (Fig. 8-51). At very low temperatures it vanishes; the temperature range most favorable for showing it appears to be between − 50 and − 100°C. Figure 8-52 shows (1) that the applied voltage must be sufficiently high so that the photonegative effect can appear and (2) that the effect occurs only for short wave-length light, *i.e.*, strongly absorbed light. The position of the transition wave-length is hardly affected by a seven-fold change in intensity. The growth of the current with time is shown in Fig. 8-53 (which is slightly modified from the original). It is evident that when

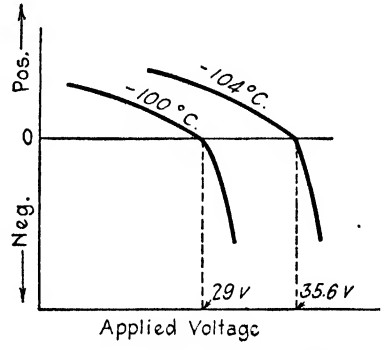


FIG. 8-51.—Photonegative effect in molybdenite.

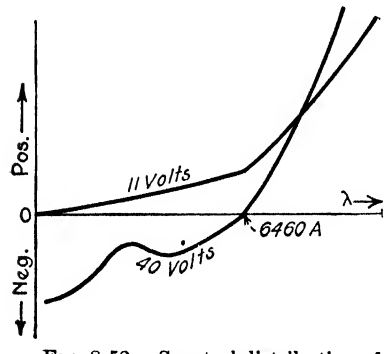


FIG. 8-52.—Spectral distribution of the photonegative effect in molybdenite at −84°C.

[1] F. SCHRÖTER and F. MICHELSSEN, "Photoelectric Cells and Their Applications; a Discussion at a joint meeting of the Physical and Optical Societies," p. 211. (Published by the Physical and Optical Societies, London, 1930.)

[2] C. RIES, *Phys. Zeits.*, **9**, 569 (1908).

[3] F. C. BROWN, *Phys. Rev.*, **33**, 1 (1911).

[4] D. S. ELLIOTT, *Phys. Rev.*, **5**, 53 (1915).

[5] W. W. COBLENTZ, *U. S. Bur. Standards, Bull.* **16**, 597 (1920).

the applied potential (21 volts) is sufficient to produce a photonegative effect, the *initial* effect of the light is to increase the conductivity.

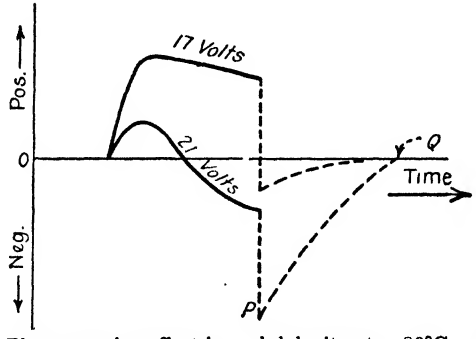


FIG. 8-53.—Photonegative effect in molybdenite at −86°C. λ = 5876A.

Immediately after cutting off the light, the dark current makes a discontinuous jump in the *negative* direction before finally settling down to the equilibrium value Q. Inasmuch as the *zero* axis merely represents the final equilibrium *deflection* corresponding to the dark current, we should note that it is probable that all negative values, even the peak P, indicate merely a temporary diminution in the dark conductivity and not a complete reversal of the direction of the current. Some investigators saw in the photonegative effect evidence for the formation by light of phases of the substance of lower intrinsic conductivity. It must be admitted that a satisfactory explanation cannot now be offered. Figure 8-53, showing that the initial effect of the light is always in the direction of increase of conductivity whether this be later diminished or reversed, hints at the formation of a space charge which, through its partial annulment of the applied field, reduced both the dark current and the photocurrent. The appearance of the effect only for the more absorbable rays seems to associate the effect with a large density of electron-releasing centers. Thus the effect may be linked in a complicated way with the differential stratification of the photocurrent, the space charge, and the non-ohmic conductivity.

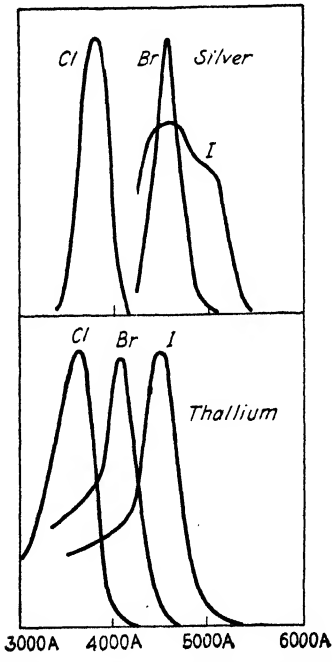


FIG. 8-54.—Photoconductivity of silver and thallium halides.

8-20. Miscellaneous Substances.—Coblentz studied the photoconductivity of the halides of thallium, lead, and silver.[1] For salts of thallium (prepared by melting on to a glass plate) the results are shown in Fig. 8-54. Lead chloride and lead bromide were insensitive. Lead iodide has a rather sharp maximum at 5200A. The results for the silver halides are also shown in Fig. 8-54. The silver chloride and bromide are photoconducting only when in a vitreous form, after cooling from the molten salt. Decomposition by light caused complications.

In 1887, Arrhenius[2] found that light, particularly blue and violet, very considerably diminished the resistance of dry thin layers of AgCl, AgBr, and AgI, which had been melted on to a glass plate and allowed to solidify. Scholl[3] found that moist thin layers of silver iodide began to be photoconducting with green light and had a maximum in the extreme violet (3700A to 4300A). It was noticed that illumination by violet light made the specimen temporarily more sensitive to the longer wave-lengths than ordinarily and that exposure to these longer wave-lengths destroyed this temporary sensitivity. This suggests an effect of the same nature as the excitation found by Gudden and Pohl in crystals. Wilson[4] exposed silver, chemically deposited, or sputtered on glass, to iodine vapor, thus producing a thin layer of silver iodide. He found that the conductivity was increased more by violet light than by ultra-violet light, which is just the opposite to that observed for the surface photoelectric effect.

Cuprous oxide (a deep-red crystalline material not to be confused with the commoner black cupric oxide) was found to be photoconducting by Pfund[5] and by Coblentz.[6] Both used an equal energy spectrum. The spectral distribution curves vary greatly with the specimen. Indeed Pfund found quite differently shaped curves, according as to whether he illuminated the specimen from the front (*i.e.*, the side to which the electrodes were attached) or from the back. The maxima were at 5400A and 6300A, respectively.

Kaempf[7] followed Volmer in the study of the photoconductivity of mercuric iodide. Kaempf used layers 0.1 mm thick which had been melted on to glass. Illumination increased the dark conductivity up to a hundredfold. In addition to showing that HgI_2 had the usual photoconductivity characteristics (*e.g.*, time lag) Kaempf used two "probe" electrodes between the principal electrodes and found that the distribu-

[1] W. W. Coblentz, *U. S. Bur. Standards, Bull.* **18**, 489 (1922).
[2] S. Arrhenius, *Sitz.-ber. d. Akad. Wiss. Wien.*, **96**, 831 (1887).
[3] H. Scholl, *Ann. d. Phys.*, **16**, 193, 417 (1905).
[4] W. Wilson, *Ann. d. Phys.*, **23**, 107 (1907).
[5] A. H. Pfund, *Phys. Rev.*, **7**, 289 (1916).
[6] W. W. Coblentz, *U. S. Bur. Standards, Bull.* **18**, 603 (1922).
[7] F. Kaempf, *Ann. d. Phys.*, **66**, 463 (1922); *Phys. Zeits.*, **23**, 420 (1922); *Zeits. f. Phys.*, **38**, 104 (1926).

tion of potential between the latter electrodes indicated a positive space charge, strong near the cathode, and changing into a relatively feeble negative space charge near the anode. This is in accordance with the view that the current is carried by electrons which crowd together as we approach the anode leaving an excess of positive charge behind (*cf.* end of Sec. **8-15**).

Rudert[1] investigated thin transparent layers of copper iodide on glass. He found the usual noticeable time lag in change of conductivity after turning the light on and off; in fact, there was no discontinuous change in conductivity at all when the light intensity was altered suddenly. The photoconductivity and the absorption increase together as we proceed along the spectrum towards the violet.

Pauli[2] found that the photoconductivity (or the "actinodielectric effect," as it was then called) in solid anthracene reached a maximum value for light of wave-length 5400A with a threshold at about 7000A. Volmer[3] also found solid anthracene to be photoconducting, but his investigations imply that the threshold is in the vicinity of 4000A. Volmer's value has been confirmed by Gudden.[4]

8-21. Selenium.—An immense amount of work has been done on the photoconductivity of selenium. Doty[5] gives a list of 1536 articles on selenium and a (selected) list of 138 patents on its applications. It must be admitted, however, that all the published results—with but one important exception—have only an empirical value in the sense that they do not disclose any significant information as to the fundamental photoelectric process which we believe to be the basis of photoconductivity. The systematic work of Gudden and Pohl shows that, only with specially selected single crystals, examined according to a certain procedure, is it possible to observe the true photoelectric current of electrons released directly by the light, without the superposition of secondary currents. Selenium is perhaps the outstanding example of a substance in which the secondary currents are of such magnitude and bewildering complexity as to mask completely the primary photoelectric current. The work of Gudden and Pohl (discussed at length in Sec. **8-7**) is unique among all the investigations on selenium in that it shows that it is possible to observe a simple primary photoelectric current uncomplicated by the presence of any secondary current. Because of the fact that none of the other investigations on selenium give any information as to the fundamental photoelectric process, we shall summarize only a few typical results very briefly.

[1] G. Rudert, *Ann. d. Phys.*, **31**, 559 (1910).

[2] W. E. Pauli, *Ann. d. Phys.*, **40**, 686 (1913).

[3] M. Volmer, *Ann. d. Phys.*, **40**, 775 (1913).

[4] B. Gudden, "Lichtelektrische Erscheinungen," p. 195 (Julius Springer, 1928).

[5] M. F. Doty, "Selenium, a List of References" (The New York Public Library, 1927).

Selenium is peculiar among the elements in that it can exist in several allotropic forms. The crystals obtained from a solution of selenium in carbon disulphide are good insulators and are somewhat transparent to red light. Gudden and Pohl observed the primary photoelectric current in this form of selenium. Conducting crystals of selenium can be obtained by condensation of the vapor. Brown and Sieg studied the photoconductivity of these crystals. Vitreous selenium, obtained by rapid cooling of molten selenium, is an insulator and shows no photoconductivity. Finally selenium, which has been "annealed" after solidification for a considerable time at a temperature between 100 and 217°C is slightly conducting in the dark, and shows considerable conduc-

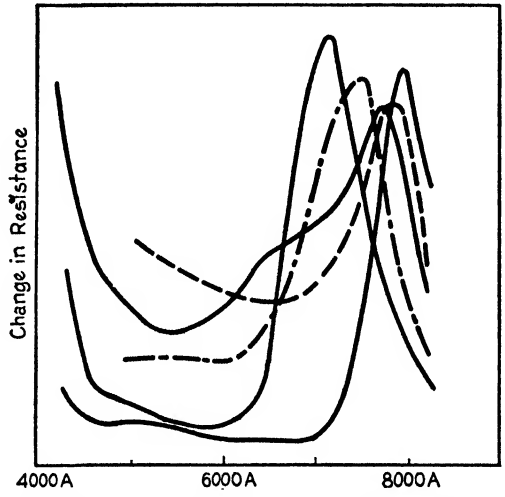


FIG. 8-55.—Photoconductivity in individual selenium crystals (each curve represents a different crystal).

tivity when illuminated. This is the kind of selenium used in "selenium cells."

Brown and Sieg[1] made an extensive study of the photoconductivity of the metallically conducting crystals condensed from selenium vapor. Some belong to the hexagonal system of crystals, some to the monoclinic. No outstanding differences in the photoconductivity of the two kinds of crystals could be found. When 0.2 mm thick, the crystals transmitted red light. The largest crystals obtained were only a few millimeters in their largest dimension. Figure 8-55 shows how the photoconductivity of these metallic crystals depends upon the wave-length of the light in an equal energy spectrum, observed after 30 sec illumination. Figure 8-56 shows the spectral distribution for a single crystal illuminated in different directions. The curves in these diagrams are far from being super-

[1] L. P. SIEG and F. C. BROWN, *Phys. Rev.*, **4**, 87 (1914); **4**, 507 (1914); **5**, 651 (1915); F. C. BROWN, *Phys. Rev.*, **5**, 167 (1915); **5**, 236 (1915).

posable, but this conclusion can be drawn: there is a maximum in all the curves between 7000A and 8000A, and there is an indication of another maximum appearing in the near ultra-violet.

8-22. Selenium Cells.—We shall consider briefly the leading characteristics of ordinary selenium cells. The form which these take is dictated largely by the use to which they are put, *viz.*, to register changes in the intensity of light incident upon them by an alteration in electrical con-

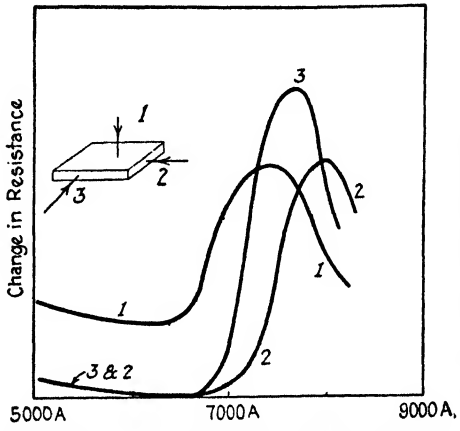


FIG. 8-56.—Effect of illuminating a selenium crystal in different directions.

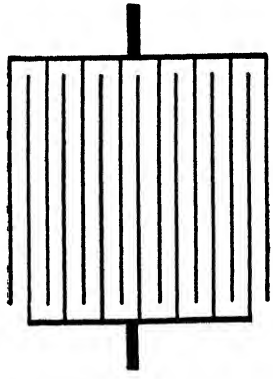


FIG. 8-57.—Electrodes in a selenium cell.

ductivity. In order to secure a relatively low total resistance for the cell (10^3 to 10^8 ohms), the electrodes are generally arranged as in Fig. 8-57, on a suitable insulating base, *e.g.*, porcelain, over which a thin layer of selenium is spread. The characteristics of the cell are largely determined by the temperature and duration of the annealing process (Piersol[1] annealed his cells at 180°C for 5 min). As a result of the annealing process, the selenium acquires a dark-gray color and develops a microcrystalline structure. (No X-ray analysis of this kind of selenium appears to be on record.) Sometimes the conductivity of the selenium cell is measured by a series arrangement of the cell, galvanometer, and battery, but more generally, because of its low resistance, a bridge arrangement is more convenient.

Investigators express their results in a variety of ways: some measure the ratio of the resistances with and without illumination; others concentrate on the change of conductivity produced by the light.[2] The change of conductivity due to the light is a function of the intensity of

[1] R. J. PIERSOL, *Phys. Rev.*, **30**, 664 (1927).

[2] Because the absorption of light is complete within a fraction of a millimeter, Piersol took special care to use very thin layers of selenium, so that there was no layer of selenium uninfluenced by the light. Consequently he obtained a current due to light (100 footcandles) a hundred times greater than the current in the dark, an unusually large ratio.

the light, its wave-length, the temperature, the time of illumination, and the applied potential. Because of the interdependence of most of these factors, it is often exasperatingly difficult to correlate the results of investigators who presumably are studying the same thing (*e.g.*, the effect of light intensity).

a. Effect of Light Intensity.—Many empirical rules have been suggested as expressing the change of conductivity as a function of the intensity of the light. If i be the additional current through the cell

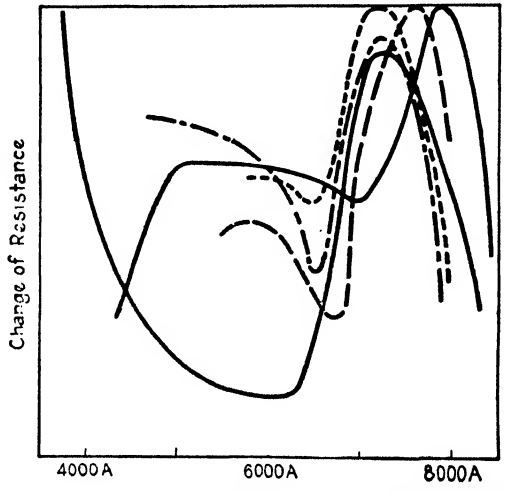


FIG. 8-58.—Photoconductivity in various selenium cells.

due to the light, and I its intensity, the various empirical relationships include the following:

$i = aI^{\frac{1}{2}}$ (Rosse, Adams, Berndt),[1] (Piersol).[2]

$i = aI^{\frac{3}{4}}$ (Hopius).[1]

$i = aI$ (Stebbins).[1]

$i = aI^x$ (Pfund).[3] $x = 0.5$, violet to yellow; $x = 1$, deep red.

$i = aI^{\frac{1}{4}}$ (Rankine).[4]

$i = aI^y$ (Barnard).[5] $0.3 > y > 0.7$. y const for any one cell.

The wide variety of results obtained is no doubt due to the fact that the variables (potential, temperature, color, etc.) which were held constant in any one investigation differed in different investigations, to say nothing of the differences between the selenium cells themselves.

b. Effect of Wave-length.—The spectral distributions of a number of commercial and other selenium cells, measured by Brown and Sieg,[6]

[1] See F. C. BROWN, *Phys. Rev.*, **33**, 101 (1911).

[2] R. J. PIERSOL, *Phys. Rev.*, **30**, 664 (1927).

[3] A. H. PFUND, *Phys. Rev.*, **34**, 370 (1912).

[4] A. O. RANKINE, *Phil. Mag.*, **39**, 482 (1920).

[5] G. P. BARNARD, *Proc. Phys. Soc. Lond.*, **40**, 240 (1928).

[6] F. C. BROWN and L. P. SIEG, *Phys. Rev.*, **4**, 48 (1914).

are shown in Fig. 8-58. The experimental conditions were: equal energy spectrum, time of illumination = 0.4 sec, applied potential not stated. Almost all the curves agree in showing a pronounced maximum sensitivity between 7000A and 8000A. A secondary maximum frequently appears in the blue and green.

c. Effect of Time.—Since a telephone receiver in series with a selenium cell which is illuminated by a beam of light interrupted 1000 times per second will give out the corresponding note, it seems clear that some response takes place within 10^{-3} sec. On the other hand, in most cells, the change in conductivity seldom attains even an approximately steady

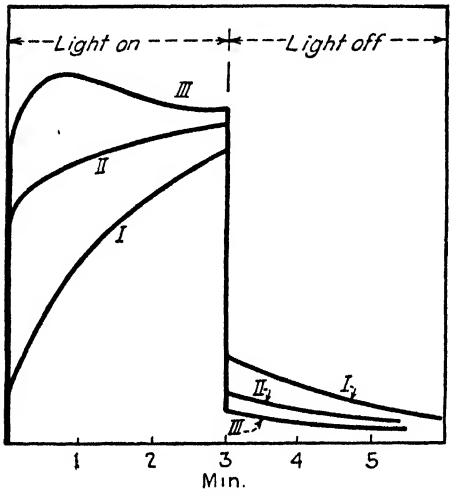


FIG. 8-59.—Current-time relations in different selenium cells.

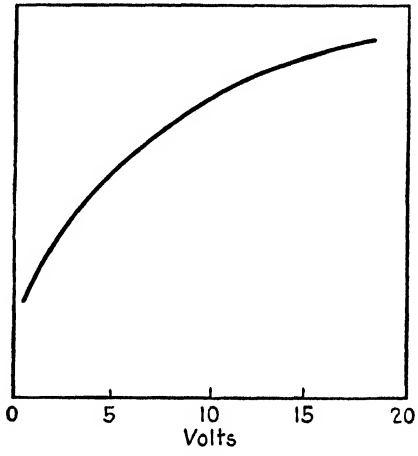


FIG. 8-60.—Current-voltage curve for a selenium cell.

end value for several minutes after the light is turned on (see Fig. 8-59 taken from C. Ries "*Das Selen*"). Barnard[1] found that the photocurrent in his selenium cells increased with the time after the illumination was begun in precisely the same way for illumination by different colors, provided that their respective intensities were adjusted to give the same photocurrent. Clearly, the conductivity of a selenium cell measured for a standard intensity must be strongly affected by the recent history of its illumination.

d. Effect of Applied Potential.—Hardly any systematic data as to the variation of photoconductivity with applied potential appear to be available. Fournier d'Albe[2] found that the resistance R of a cell, whether illuminated or not, depended upon the potential V according to the equation $R = a - b \log V$, where a and b are constants. His results are shown graphically in Fig. 8-60.

[1] G. P. BARNARD, *Proc. Phys. Soc. Lond.*, **40**, 240 (1928).
[2] E. E. FOURNIER D'ALBE, *Proc. Roy. Soc.*, **86**, 452 (1912).

e. Effect of Temperature.—Piersol[1] found that the dark current through a certain selenium cell dropped from 10^{-3} amp to 5×10^{-10} amp when the temperature was changed from 10 to $-180°C$. The current due to illumination (100 footcandles) changed only from 6×10^{-3} amp to 5×10^{-3} amp for the same temperature drop.

8-23. The Photographic Latent Image and Photoconductivity.—The formation of the latent image in photographic emulsions by light is closely related to photoconductivity. Although the term latent image

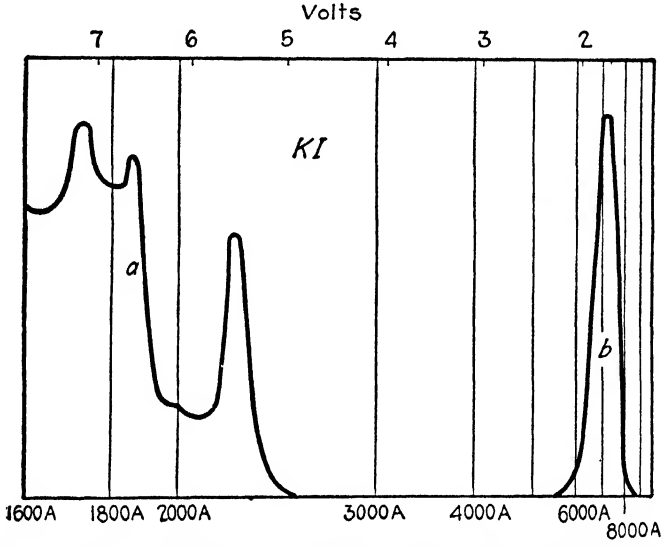


FIG. 8-61.—Absorption spectra of potassium iodide. (*a*) Characteristic absorption band. (*b*) Induced absorption band. (For *a* and *b* to be comparable, the ordinates of *a* must be multiplied by 10^6.)

has hitherto been associated only with the silver halides used in emulsions, we shall, following Hilsch and Pohl,[2] consider it to apply also to the alkali halides in which certain of its aspects can be investigated with less difficulty than in the silver halides.

A crystal of a pure alkali halide is perfectly transparent in the near infra-red and in the visible. It has no measurable absorption until we get well into the ultra-violet. (For the iodides, bromides, and chlorides, the absorption begins approximately at 2500A, 2200A, and < 2000A, respectively.) The absorption spectrum of KI (and indeed of any other alkali iodide) is shown at the left of Fig. 8-61. It is probable that a somewhat similar pattern, shifted to shorter wave-lengths, would be found for the bromides and chlorides, if it were possible to carry out the measurements in this almost inaccessible region of the ultra-violet.

[1] R. J. PIERSOL, *Phys. Rev.*, **30**, 664 (1927).

[2] R. HILSCH and R. W. POHL, *Zeits. f. Phys.*, **57**, 145 (1929); **59**, 812 (1930); **64**, 606 (1930).

When ultra-violet light within the absorption band is absorbed by the crystal, the previously clear crystal becomes colored and a new absorption band appears in the visible or near infra-red.[1] The first absorption band, which is permanent, we shall designate as the *characteristic absorption band;* the second absorption band we shall designate as the *induced absorption band.* The induced absorption band has a simple bell-like shape. For KI, it has a maximum at 7200A (Fig. 8-61); while for NaCl, the maximum is at 4700A. The positions of the induced absorption

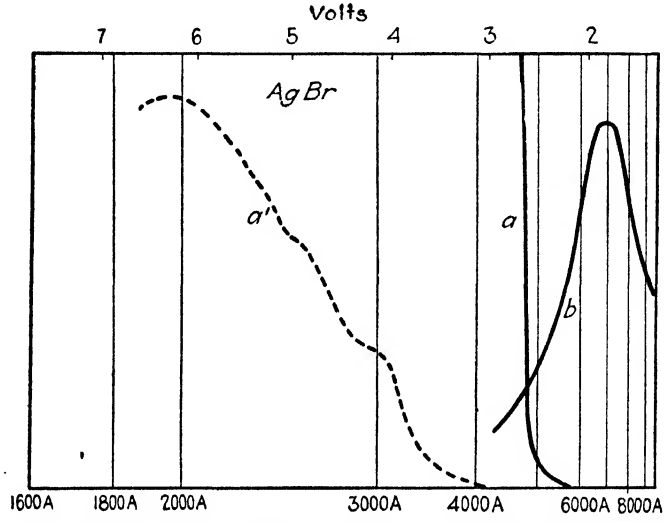


FIG. 8-62.—Absorption spectra of silver bromide. (*a*) Characteristic absorption band. (*b*) Induced absorption band. (*a'*) Same as *a*, reduced by a factor of about 10^6.

bands for the other alkali halides will be found in a paper by Ottmer.[2] The typical photographic material AgBr has similar bands (Fig. 8-62). The only difference between the silver halides and the alkali halides is that in the case of the silver halides there is some overlapping between the characteristic band and the induced band, while in the case of the alkali halides there is a complete separation.

Exactly analogous effects were obtained by Kirillow[3] who investigated the absorption of light by granular layers of various silver halides and found new absorption bands to appear on the long wave-length side of the characteristic absorption band. There is a considerable lack of agreement between his curves and those of Hilsch and Pohl as regards shape and position of maxima. This is no doubt due in some way to the fact that in one investigation single crystals were used, while in the other a layer composed of many small crystals was used. For AgCl, AgBr, and AgI he found characteristic absorption maxima at 3840A, 4300A, and 4250A, and induced absorption maxima at 5050A, 5720A, and 6500A, respectively.

[1] R. HILSCH and R. W. POHL, *Zeits. f. Phys.*, **57**, 145 (1929); **59**, 812 (1930); **64**, 606 (1930).

[2] R. OTTMER, *Zeits. f. Phys.*, **46**, 798 (1928).

[3] E. A. KIRILLOW, *Zeits. f. Wiss. Photog.*, **26**, 235 (1929).

Precisely the same induced absorption band is produced in clear NaCl crystals (*a*) by ultra-violet light, (*b*) by X-rays, and (*c*) by exposure to Na vapor. The last method of producing the induced band lends support to the view that the induced band is due to free neutral metal atoms distributed throughout the lattice. That neutral Ag atoms appear in the lattice after illumination was first suggested by Sheppard and Trivelli[1] and by Fajans[2] to account for the effect of light on AgBr, that is, to describe the nature of the latent image. In the unilluminated crystal the metal M and the halogen H are both charged ions. The effect of the absorption of light may be represented by

$$M^+H^- \rightarrow M + H \tag{8-14}$$

In the case of AgBr it has been found that free bromine and free silver appear as a result of the absorption of light. Eggert and Noddack[3] and Kieser[4] found that for every quantum of light absorbed by the layer of AgBr approximately one silver atom was set free.[5] We thus have satisfactory evidence in support of the view that the induced absorption band is due to the neutral atoms in the lattice, whether they be formed by the absorption of light in the characteristic absorption band, or by the absorption of X-rays, or by direct diffusion of neutral metal atoms into the lattice. Smakula[6] found that approximately one quantum of light in the characteristic absorption band had to be absorbed to produce a single neutral atom. The number of neutral atoms produced was calculated from the intensity of the induced absorption band. (Smakula used KBr, KI, RbBr, and RbCl in his investigations.)

As was mentioned in the last paragraph, the formation of the photographic latent image has been attributed to the appearance of free neutral atoms of Ag. The latent image is, as its name implies, invisible. By a suitable chemical process—development—each isolated Ag atom may be made the nucleus around which more Ag atoms are deposited, thus leading to a visible image. While important technologically, the development of the latent image does not help us to understand the fundamental process, and so we shall not discuss it any further. In a remarkably interesting investigation, Hilsch and Pohl[7] have shown that, under proper experimental conditions, the latent image can be revealed by its

[1] S. E. Sheppard and A. P. H. Trivelli, *Photog. Jour.*, **61**, 403 (1921).

[2] K. Fajans, *Chem. Ztg.*, **45**, 666 (1921); *Zeits. f. Elektrochem.*, **28**, 299 (1922).

[3] J. Eggert and W. Noddack, *Zeits. f. Phys.*, **20**, 299 (1924).

[4] H. Kieser, *Zeits. f. Wiss. Photog.*, **26**, 321 (1929).

[5] For criticisms of this conclusion see G. B. Kistiakowsky, "Photochemical Processes," pp. 41–51 (The Chemical Catalogue Company, 1928), and also a summary by J. Eggert and W. Noddack, *Zeits. f. Phys.*, **58**, 861 (1929).

[6] A. Smakula, *Zeits. f. Phys.*, **63**, 762 (1930).

[7] R. Hilsch and R. W. Pohl, *Nachr. d. Ges. d. Wiss. zu Göttingen*, Math.-phys. Klasse, p. 176, 1930; *Zeits. f. Phys.*, **64**, 606 (1930).

characteristic color, and that its spectrum is identical with that of the induced absorption band. In other words, the neutral metal atoms, forming the latent image, are those which are responsible for the induced absorption band and it would be quite correct to refer to this band as the absorption spectrum of the latent image itself. An ordinary photographic emulsion (20μ thick) containing AgBr equivalent to a layer 2.5μ thick is practically totally opaque to 4000A. (This is presumably because of the repeated internal reflections within the mass of tiny crystals embedded in the emulsion.) A developable latent image was obtained in such an emulsion as a result of an exposure of 0.02 sec to light of wave-length 4000A, whose intensity was $2 \cdot 10^3$ quanta/cm^{2}sec. A single crystal of AgBr, 1.8 cm thick, was also found to be practically opaque to light of the same wave-length. Now, in order that the average *density* of neutral Ag atoms set free in the crystal shall be the same as that in the emulsion when they are illuminated by the same light, the exposure for the crystal must be $1800/2.5 = 720$ times as long. This is 14 sec. Hilsch and Pohl found that exposing the crystal of AgBr (1.8 mm thick) to the light for 14 sec produced a measurable induced absorption band, similar to that shown in Fig. 8–62. Thus they showed that the distribution of free Ag atoms corresponding to a developable latent image has a measurable absorption. Absolute measurements of this absorption showed approximate quantum equivalence between the number of quanta absorbed and the number of Ag atoms made neutral.

We shall now consider the matter of absorption of light *within* the induced absorption band. In the case of colored NaCl—the color being that due to the induced absorption band—we saw in Sec. **8-10** that absorption of light results in photoconductivity and in "excitation." When excitation occurs, the absorption curve is flattened out and extended on the long wave-length side (Fig. 8-28). Absorption of red or infra-red light in this extension causes a disappearance of the excitation and the curve returns to its normal shape. This reversible effect is well marked in colored NaCl. In most substances, however, absorption of light in the induced absorption band leads to a mixture of excitation and another effect called "bleaching." The first is a reversible process; the latter is irreversible. A natural explanation is that in both cases light releases a photoelectron from a neutral metal atom. If this photoelectron is captured by a neutral halogen atom and the metal atom becomes an ion, we once more revert to the state in which ions replace the neutral atoms, and so the induced absorption spectrum disappears. Hence the irreversible bleaching effect. On the other hand, the reversible phenomenon of excitation has been explained by Gudden and Pohl (Sec. **8-10** and **8-11**) in this way. The absorption of a quantum results in the ejection of an electron from the neutral metal atom, or "center,"

leaving it an ion. It immediately becomes neutral again by taking an electron from its surroundings. Thus a positive charge builds up around the neutral atom and it is this which accounts for the excitation, *i.e.*, the distortion of the induced absorption band. Removal of this accumulation of positive charges by warming or by infra-red light results in the disappearance of the excitation. Smakula[1] found that the ratio of bleaching to excitation depended largely on the crystal studied and on its temperature. The silver halides, for example, show no reversible effects when light is absorbed in the induced absorption band. The effect is entirely one of irreversible bleaching. This will be recognized as the fundamental cause of the Herschell effect, which is that flooding a photographic plate (before development, of course) with infra-red light destroys the latent image. Smakula found approximate quantum equivalence between the number of quanta absorbed in the induced absorption band and the total number of atomic events involving excitation and bleaching.

The appearance of the induced absorption band seems to call for irregularities in the crystal. There is some evidence, shortly to be discussed, that the electrons bound to those halogen ions, which form part of the normal lattice, cannot be set free by the energy associated with the quanta actually effective. An escape from this difficulty is provided by the hypothesis of Fajans,[2] who supposes that the electrons are detached from the halogen ions located at the submicroscopic flaws in the crystal where the binding forces are less than normal. Then again, while electrons pass through a perfect crystal without difficulty, they may easily recombine with metal ions situated at the flaws to form the neutral atoms. This is in accord with the view of Sheppard, Trivelli, and Loveland, who maintain that the great sensitivity of photographic emulsions is to be attributed to the presence of minute "specks" of Ag_2S (possibly containing free Ag distributed on, or within, the grains of AgBr). These specks distort the lattice in their immediate vicinity, thus providing just those conditions which enable a quantum of relatively low energy to separate an electron from a bromine ion. (A definite threshold for this effect is therefore not to be expected.)

Podaschewsky[3] found that the photoconductivity of colored NaCl diminished with increasing plastic deformation, brought about by pressure, bending, etc. At the same time progressive bleaching was observed. The effect of plastic deformation is clearly to make it possible for the neutral Na and Cl atoms to change into ions as the result of a photoelectric effect at the Na atom, thus replacing reversible excitation by irreversible bleaching.

[1] A. Smakula, *Zeits. f. Phys.*, **59**, 603 (1929).
[2] K. Fajans and W. Frankenburger, *Zeits. f. Phys. Chem.*, **105**, 253 (1923).
[3] M. N. Podaschewsky, *Zeits. f. Phys.*, **50**, 369 (1929); **65**, 799 (1930).

Various attempts have been made to compute the minimum energy necessary to form the latent image. Since the latent image is made up of neutral atoms, it has been suggested that the heat of decomposition of solid AgBr should lead to a value for the photographic threshold. The heat of decomposition is 25 kg-cal/mol, which corresponds to a quantum of wave-length 11,000A. The threshold for the formation of the latent image in a carefully prepared emulsion of pure AgBr is, however, 5200A. It is probable, therefore, that we have to consider the energies involved in the individual steps in the process described by Eq. (8-14). The two steps are represented by

$$\begin{aligned} H^- + h\nu &= H + \text{electron} \\ M^+ + \text{electron} &= M. \end{aligned} \tag{8-15}$$

The energy required to detach an electron from an isolated Br ion is E, its electron affinity. The halogen ion is, however, in a lattice, and its nearest neighbors are positive ions. This will increase the energy to detach the electron by an amount φe, the electrostatic energy of the lattice. Experimentally, however, $E + \varphi e$ is much too large, for it corresponds to a wave-length far shorter than that of the threshold for any crystal investigated. It is therefore necessary to look for some quantity X which will give the right value for the threshold frequency in

$$h\nu = E + \varphi e - X. \tag{8-16}$$

The introduction of X is reasonable because $E + \varphi e$ measures the work necessary to remove an electron to infinity. For X, Pauling[1] substitutes the electron affinity of the crystal as a whole, *i.e.*, the work done when an electron is brought into the crystal from infinity. Fajans, and Hilsch and Pohl[2] replace X by J_a, the ionization potential of the metal atom, because the process ends up with a neutral metal atom. These and other proposals for X are discussed thoroughly by Sheppard and Vanselow.[3] On account of the considerable uncertainty in the values of the constants involved, it is impossible to decide definitely whether or not the formulas proposed give an adequate account of the process.

The alternative hypothesis of Fajans, locating those halogen ions which lose electrons at the irregularities in the crystal, where the values of φe are smaller than the normal value for ions in the regular lattice by an indefinite amount, cannot be tested quantitatively.

The hypothesis that the latent image is formed as a result of the release of an electron by light obviously suggests identity between the region of the spectrum effective photoelectrically, and that effective photographically. It is found, however, that the threshold of the surface photoelectric effect of a photographic material is much farther to the ultra-violet than the spectral region known to produce a latent image. The difference is due to the work function at the surface, for an electron liberated within the material may not have enough energy to pass through the surface. Closer correlation with the photoconductivity of the material is to be expected, and is actually found to exist. The discrepancies that still remain are no doubt to be attributed to the fact that, as a rule, when the photographic effect of AgBr is being investigated, it is

[1] L. Pauling, *Phys. Rev.*, **34**, 954 (1929).

[2] R. Hilsch and R. W. Pohl, *Zeits. f. Phys.*, **57**, 145 (1929).

[3] S. E. Sheppard and W. Vanselow, *Jour. Phys. Chem.*, **33**, 250 (1929); **34**, 2719 (1930).

in the form of a layer of microcrystals usually held together by gelatine, while when the photoconductivity is being measured, the AgBr is generally either a large single crystal or a layer solidified after melting. Some typical results are assembled in Table (8-2).

TABLE 8-2.—PHOTOEFFECTS IN SILVER SALTS[1]

I	II	III	IV	V	VI
Silver salts	Threshold of the surface photoelectric effect[2]	Photoconductivity		Photographic threshold	Threshold of characteristic absorption band[1,4]
		Threshold	Maximum[3]		
AgI	4070A	5300A	4250A	4500A	5200A
AgBr	3320A	4800A	4300A	5200A	4700A
AgCl	3130A	4100A	3840A		4100A

[1] Where no reference is given in the table, see S. E. Sheppard and W. Vanselow, *Jour. Phys. Chem.* **34**, 2719 (1930).

[2] F. G. Toy, H. A. Edgerton, and J. O. Vick, *Phil. Mag.*, **3**, 482 (1927); F. Krüger and A. Ball *Zeits. f. Phys.*, **55**, 28 (1929).

[3] E. A. Kirillow, *Zeits. f. Wiss. Photog.*, **26**, 235 (1929).

[4] R. Hilsch and R. W. Pohl, *Zeits. f. Phys.*, **48**, 384 (1928).

Fajans[1] and Toy[2] have both shown that the same spectral region is effective in producing photoconductivity and decomposition in silver halides. There is therefore but little doubt, in view of all the evidence assembled, that the fundamental photographic process (the formation of the latent image) is due to electrons set free in the lattice combining with Ag ions to form Ag atoms.

Toy and Harrison[3] found that the current in a thin layer of AgBr attained its full value in 0.07 sec, and that it was strictly proportional to the intensity of the light. Although strict proportionality is a characteristic of the primary photoelectric current, the finite time for the starting of the current, together with the fact that the AgBr was a layer of many tiny crystals fused together, and not a single crystal, make it extremely probable that secondary currents were being measured.

Trivelli[4] saw in the failure of the reciprocity law for the blackening of the photographic plate a reason for associating the photographic effect with the secondary currents of Gudden and Pohl rather than with the primary photoelectric currents. But the discovery of quantum equivalence between the amount of light absorbed and the amount of silver set free implies a very direct correlation with the primary photoelectric

[1] K. Fajans, *Zeits. f. Electrochem.*, **28**, 499 (1922).

[2] F. C. Toy, *Proc. VII. Intern. Cong. Photog.*, p. 23 (1928).

[3] F. C. Toy and G. B. Harrison, *Proc. Roy. Soc.*, **127**, 613 (1930).

[4] A. P. H. Trivelli, *Jour. Franklin Inst.*, **204**, 649 (1927).

effect in which quantum equivalence is an outstanding characteristic. It may perhaps be argued that there is no correlation between secondary currents and the formation of the visible image, except in so far as they are both ultimately dependent on a photoelectric liberation of electrons. Beyond this point, the secondary currents depend on the change in the conductivity of the lattice produced by the freeing of electrons and upon the applied potential, while the formation of the visible image depends upon the chain of events occurring during development. It seems, therefore, unlikely that there should be any connection between the density of a visible image and the photoconductivity of the emulsion.

8-24. Phosphorescence: General Characteristics.—There is one group of phosphorescent substances in which it is found that the phosphorescence of the substance is intimately related to its photoelectric properties. Indeed the photoelectric separation of an electron from its parent atom appears to be a necessary condition for the appearance of this kind of phosphorescence.[1] These substances are generally known as *phosphors*, sometimes as *Lenard phosphors* because of the immense amount of work done on them by Lenard.[2] A typical phosphor, CaBiS, is obtained by melting a mixture of calcium sulphide, a trace of bismuth, and sodium sulphate. In general, a phosphor is made up of

$$AH + \text{a flux} + \text{trace of } M,$$

where

A may be Ca, Ba, Sr, Mg, Be, or Zn.
H may be S or Se.
M may be Bi, Mn, Fe, Co, Ni, Cu, Zn, Ag, Sn, Sb, Pb, or Ca.

The flux may be Na_2SO_4, $Na_2B_4O_7$, or NaCl.

The phosphorescence depends upon the presence of minute quantities of M (the "heavy metal"). The omission of M—provided that the other constituents are extremely pure—causes the phosphorescence to disappear. The notation (CaBiS) is self-evident.

The phosphorescent properties of these phosphors, in so far as they have significance photoelectrically, may be summarized as follows. A phosphor gives out independent emission bands of phosphorescent light, each with its characteristic rate of decay. Thus we have the designations: CaBiS-α, CaBiS-β, . . . bands for a CaBiS phosphor. The rate of emission of light is greatly increased by rise of temperature.

[1] It is to be recorded that this is the only group of phosphorescent substances in which a correlation with the photoelectric effect has been found. No correlation whatever exists in the case of many other groups of phosphorescent substances (the uranyl salts, the platinocyanides, and the phosphorescent organic compounds). It may be that, in these groups, phosphorescence is not conditioned by a complete separation of an electron from an atom. Excitation of the atom (in the sense used when light is absorbed by gaseous atoms) may be sufficient.

[2] P. Lenard and V. Klatt, *Ann. d. Phys.*, **15**, 671 (1904).

At liquid-air temperature, the emission is almost completely arrested. The "total light," *i.e.*, the integral of the intensity of phosphorescence over the time until the phosphorescence has completely ceased, is constant no matter whether the phosphorescence is all over in a fraction of a second at high temperatures, or whether it takes days at a lower temperature.[1] Illumination with red or infra-red light accelerates the return of the phosphor to its initial state. This return may, or may not, be accompanied by the emission of the phosphorescent light which normally occurs in the absence of long wave-length illumination. In the first case, when the return is accompanied by a faster emission of the phosphorescent light, the process may be termed *accelerated phosphorescence.* In the second case, when the return takes place unaccompanied by phosphorescence, we have *quenching.*[2] (Here the stored up energy is no doubt converted into heat instead of being radiated. A somewhat analogous process is that of the "quenching" of resonance radiation from mercury vapor by hydrogen, which causes the energy of excitation to be diverted from radiation into another effect—dissociation of the hydrogen.) The proportion of the accelerated phosphorescence to the quenching depends greatly on the nature of the phosphor, and, to some extent, on the wave-length of the long wave-length light used. (The spectral distribution of the two processes sometimes overlaps considerably, *i.e.*, the same wave-length may produce both effects.) In some phosphors there is no quenching; the long wave-length light therefore releases all the stored up energy as phosphorescence. The spectral distribution for the absorption of light by an excited phosphor is broadened toward long wave-lengths as compared with that for an unexcited phosphor. The absorption of light in this region where the absorption is temporarily increased does not result in carrying the substance to a higher state of excitation, but, on the contrary, rapidly removes the excitation and brings the phosphor back to its normal state. The striking parallelism between this process and the results we have discussed in connection with the photoelectric effect in colored rocksalt, for example, is evident.

The efficiency p of a phosphor may be defined as the ratio of the energy of the phosphorescent light to the energy of the exciting light (*i.e.*, the absorbed light). It is found that this efficiency is in close agreement with the view that one quantum of phosphorescent light is associated with one quantum of absorbed light, according to the following equation

$$p = \frac{h\nu_e}{h\nu_a} = \frac{\lambda_a}{\lambda_e},$$

[1] P. Pringsheim, "Fluorescenz und Phosphorescenz," p. 158 (Julius Springer, 1928).

[2] The terms "accelerated phosphorescence" and "quenching" are introduced here to denote the processes which Lenard has named *Ausleuchtung* and *Tilgung*, respectively.

where the suffices e and a refer to emission and absorption, respectively. Typical results, due to Schmieder,[1] are shown in Table 8-3.

TABLE 8-3.—EFFICIENCY OF PHOSPHORS

Phosphor	Mean λ_e of the phosphorescent light	λ_a for the exciting light	p observed	p calculated
CaBiS	4400A	4350A	0.97	0.99
		3650A	0.82	0.83
ZnCuS	5150A	4350A	0.84	0.85
		3650A	0.73	0.71
CaCuS	5250A	4350A	0.76	0.85
		3650A	0.64	0.70

Lenard[2] put forward a theory that the phosphorescence was not a property of the phosphor as a whole, but was conditioned by relatively few "centers" which contained the atoms of the foreign metal. The exciting light separates an electron from its parent atom in a center and it gets tangled in the vicinity. The center is now excited and its absorption spectrum altered. The return of the electron to its parent atom, or, at any rate, its replacement by another, causes the emission of a quantum. At low temperatures, when the insulation is relatively very high, the electron return or replacement is suppressed, at higher temperatures the return is accelerated, increasing the intensity of phosphorescence. Except for the fact that Lenard thought it necessary to postulate that the displaced electron does not get outside the center in which it originates, the theory is ready for linking with the photoelectric effect. This brief account of phosphors must suffice. A very comprehensive account will be found in the *Handbuch der Experimentalphysik*, Vol. XXIII. A concise and useful summary is to be found in Pringsheim's "Fluorescenz und Phosphorescenz," Chapters VI and IX.

8-25. Phosphorescence: Photoelectric Aspect.—Elster and Geitel[3] found that certain phosphors (*e.g.*, Balmain's paint) had a relatively high surface photoelectric effect. Lenard and Saeland[2] discovered that the long wave-length limit of the light for exciting phosphorescence coincided with that for producing a surface photoelectric effect. Goggel[4] found that in two different phosphors the wave-length which produced the maximum surface photoelectric effect also produced the maximum phosphorescence. These results point to a close connection between the photoelectric effect and phosphorescence, though one would expect,

[1] F. SCHMIEDER, *Ann. d. Phys.*, **77**, 381 (1925).
[2] P. LENARD and S. SAELAND, *Ann. d. Phys.*, **28**, 476 (1909).
[3] J. ELSTER and H. GEITEL, *Ann. d. Phys.*, **44**, 722 (1891).
[4] K. GÖGGEL, *Ann. d. Phys.*, **67**, 301 (1922).

in the last two cases, a displacement of the wave-lengths for the photoelectric effect towards shorter wave-lengths because of the surface work function. Lenard[1] did not consider that a close connection could be established between photoconductivity within a phosphor and its phosphorescence.

In a series of investigations, Gudden and Pohl[2] showed that the photoconductivity and phosphorescence in phosphors were closely related. That pulverized phosphors are crystals can be shown by X-rays; the photoconductivity observed is therefore characteristic of a mass of small crystals. Gudden and Pohl found that the maxima in the spectral distribution of the light causing photoconductivity coincided with the maxima found by Lenard for the excitation of phosphorescence. This result could be obtained with field strengths of the order of 5000 to 16,000 volts/cm. Fields around 1000 volts/cm, such as Lenard used, do not reveal these maxima. The accelerated phosphorescence, due to long wave-length light, is associated with the positive primary photoelectric current.[3] A ZnMnS phosphor was suitably excited in a strong electric field (10^4 volts/cm). After 30 sec in the dark, at the end of which no appreciable current flowed, it was illuminated by infra-red light and the galvanometer indicated the passage of a quantity of electricity whose amount was larger, the larger the previous excitation. Thus the movement of electrons to replace the electrons ejected from the centers during excitation is to be regarded as both the positive primary photoelectric current and the cause of the accelerated phosphorescence. Except at very low temperature, the phosphorescence occurs spontaneously (though much less intense than when accelerated by infra-red light) and a correspondingly small positive photoelectric current is associated with it.

When it is recalled that the phosphor is not a single crystal but a mass of tiny crystals packed together, it is evident that the currents ordinarily observed in these investigations are secondary currents, which, in turn, are conditioned by the presence of the photoelectric current. Hence the characteristic slow rise and fall of the observed current. To avoid secondary currents, Gudden and Pohl in one investigation mounted the phosphor between two strips of metal 0.1 mm apart, and applied a small potential (100 volts). The current now started and stopped instantly with the illumination just as a photoelectric current should. On flooding the phosphor with red light during the illumination by the exciting light, the current was approximately doubled. This

[1] P. Lenard, *Sitz.-ber. d. Heidelberg. Akad. d. Wiss.* (A), **8**, 80 (1918); P. Pringsheim, *loc. cit.*, p. 182.

[2] B. Gudden and R. Pohl, *Zeits. f. Phys.*, **1**, 365 (1920); **2**, 181 (1920); **2**, 191 (1920); **3**, 98 (1920); **4**, 206 (1921); **31**, 651 (1925); **35**, 254 (1925).

[3] B. Gudden and R. Pohl, *Zeits. f. Phys.*, **3**, 98 (1920).

happened whether the phosphor showed strong quenching as in the case of ZnCuS, or strong accelerated phosphorescence as in the case of ZnMnS. The results therefore indicate that in both cases the red light promotes the flow of the positive primary current resulting in the loss of excitation by the centers.[1] This process is fundamental to all photoelectrically conducting crystals of which the phosphors are merely one particular type. The removal of the electron from the center during the process of excitation is revealed electrically as the electron primary current. The replacement of the electron in the center is revealed as the positive primary current. Whether the full yield of phosphorescence is obtained or not, during the replacement of the electrons due to long wave-length illumination, merely depends on the particular phosphor investigated. Hence the effect of infra-red illumination on the phosphorescence has less significance in revealing the nature of the fundamental photoelectric process than its effect on the observed currents.

The yield of phosphorescence, *i.e.*, the ratio of the energy emitted to that absorbed, in some cases approaches unity.[2] Rupp[3] found that the "total light" (*i.e.*, phosphorescence) radiated when the accelerated phosphorescence was produced by heat was strictly proportional to the amount of electricity transported. In some cases the ratio (quanta emitted): (electrons made free) was of the order unity.

Since the photoconductivity of colored rocksalt and that of phosphors are both conditioned by the presence of foreign atoms in the lattice, one might expect phosphorescence in colored rocksalt. Pohl and Rupp[4] have investigated the phosphorescence in various alkali halides containing foreign atoms. In such substances the light absorption and the electrical conductivity are easily studied, but the emission of phosphorescent light is generally very small. Four kinds of light absorption in such phosphors may be distinguished:

1. Taking rocksalt as a typical pure crystal of this class, its absorption is zero right up to 1800A.

2. The rocksalt may be colored yellow or green by (*a*) electron bombardment, (*b*) X-rays, or (*c*) heating in Na vapor. An induced absorption spectrum now appears in the visible (Fig. 8-28).

3. A trace of a foreign metal (*e.g.*, Pb, Tl, Cu, Ag) halide may be added to the molten rocksalt which is then crystallized. (Fuller details are given by Hilsch.[5]) The absorption is now changed by the addition

[1] It is stated by Gudden and Pohl (*Zeits. f. Phys.*, **21**, 1 [1924]) that the secondary currents diminish extraordinarily under long wave-length illumination. This is as it should be, for the secondary currents are conditioned by excitation which is destroyed by red light.

[2] P. Lenard, *Sitz.-ber. d. Heidelberg. Akad. d. Wiss.*, **13**, 68 (1917).

[3] E. Rupp, *Ann. d. Phys.*, **70**, 391 (1920).

[4] R. Pohl and E. Rupp, *Ann. d. Phys.*, **81**, 1161 (1926).

[5] R. Hilsch, *Zeits. f. Phys.*, **44**, 421, 860 (1927).

of a new narrow band (Fig. 8-63) which we naturally attribute to the foreign metal.

4. Rocksalt may be colored blue by colloidal particles of sodium dispersed throughout it.

No phosphorescence could be detected in 1. A weak phosphorescence was observed in 2 and 4. Very strong phosphorescence and also marked photoelectric conductivity appeared in 3. The discovery that traces of certain metals (Pb, Tl, Cu, Ag) dispersed throughout a NaCl or a KCl crystal produce a single characteristic narrow absorption band in the region where the base material is perfectly transparent may prove of great value in revealing quantitative relationships between the light absorption, the photoelectric effect, and phosphorescence.

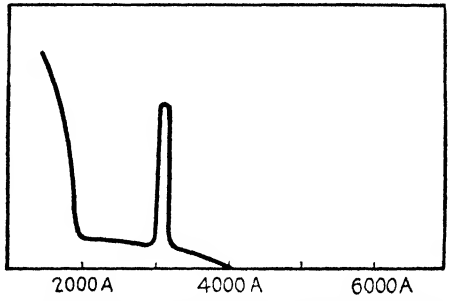


FIG. 8-63.—Absorption of rocksalt containing a trace of thallium chloride.

Gudden and Pohl[1] found that illuminating a ZnCuS phosphor with intense light approximately doubled its dielectric constant. An apparent change in the dielectric constant may be accounted for by an increased local conductivity in isolated centers; hence we may expect a correlation between a photoelectric effect and a change in the dielectric constant in phosphors.

PHOTOCONDUCTIVITY IN LIQUIDS

That insulating liquids (such as petroleum ether, carbon tetrachloride, benzol, etc.) can be made conducting by exposure to X-rays and γ-rays was discovered many years ago.[2] The conductivity imparted to such liquids by the radiation has many characteristics in common with those found in ionized gases. Owing to the extremely small mobility and low recombination coefficient of the ions, however, very noticeable time lags are observed. The current usually takes 2 or 3 hr after the illumination is begun to attain its equilibrium value, and the same length of time to decrease to zero after the illumination is cut off. When due allowance is made for these time lags, it is found that the current-potential curves for ionization in liquids resemble those found in gases, in that saturation currents can be obtained at sufficiently high fields. The existence of the surface photoelectric effect for metals extending from the X-ray region up to a definite threshold in the ultra-violet or in the visible, leads us to

[1] B. GUDDEN and R. POHL, *Zeits. f. Phys.*, **1**, 365 (1920).

[2] J. J. THOMSON, *Nature*, **53**, 378 (1895); **55**, 606 (1897); P. CURIE, *Comptes Rend.*, **134**, 420 (1903); G. JAFFÉ, *Ann. d. Phys.*, **32**, 148 (1910); **42**, 303 (1913).

ask whether or not the photoconductivity of insulating liquids extends up to the same region. The results to be discussed in the next section show that certain liquids are rendered photoconducting by ultra-violet light.

8-26. Photoconducting Liquids.—Goldmann found no conductivity change in alcoholic solutions of dyes (*e.g.*, eosin) due to illumination by visible light.[1] The excitation of fluorescence in such solutions cannot, therefore, be associated with the freeing of electrons. Byk and Borck found that a solution of anthracene in hexane, purified electrolytically until the conductivity in the dark was negligible, became photoconducting when illuminated by light passed through a quartz plate from a carbon arc, provided that the solution was saturated.[2] When unsaturated, no photoconductivity could be measured.

Volmer confirmed this result so long as the wave-length of the light used was between 2250A and 4000A.[3] If light of shorter wave-length than 2250A were used, then photoconductivity was obtained in unsaturated solutions as well. There appear to be two distinct effects. One is a genuine volume photoelectric effect with a threshold at 2250A, and the other is a conductivity apparently arising from the passage into the solution of positive and negative ions, perhaps formed photochemically in the extremely thin layers of anthracene precipitated on the surfaces of the electrodes. (A similar effect was found with sulphur in hexane. Here, however, the evidence indicated that only the positive ions went into solution.) When the solution is unsaturated, there are no such layers of solid anthracene and no conductivity. There is therefore no real *volume* photoelectric effect in the solution with wave-lengths longer than 2250A. When light of wave-length shorter than 2250A was used, the slightest trace of anthracene in hexane produced a very marked increase in conductivity on illumination, the order being 100- to 300-fold. The conductivity was directly proportional to the amount of liquid illuminated. As the applied potential was increased, the current became almost saturated in the region between 300 and 700 volts. The maximum conductivity occurred, in the particular form of cell used, when the concentration of the anthracene was 0.00025 normal. Greater concentrations caused the light to be completely absorbed in too thin a layer close to the quartz window.

In Sec. **8-20** it was mentioned that the threshold for photoconductivity in solid anthracene was approximately 4000A. The threshold for the surface photoelectric effect in solid anthracene is about 2250A.[4] It is curious that the threshold for the photoconductivity of a solution of

[1] A. Goldmann, *Ann. d. Phys.*, **27**, 449 (1908).
[2] A. Byk and H. Borck, *Verh. d. Deutsch. Phys. Ges.*, **12**, 621 (1910).
[3] M. Volmer, *Ann. d. Phys.*, **40**, 775 (1913).
[4] M. Volmer, *loc. cit.*; A. L. Hughes, *Phil. Mag.*, **24**, 380 (1912).

anthracene in hexane should be so much closer to the threshold for the surface photoelectric effect in solid anthracene than to the threshold for its photoconductivity. On the other hand, there may be significance in the fact that the peculiar kind of conductivity observed by Volmer only in *saturated* solutions and the photoconductivity in solid anthracene are apparently excited by the same spectral region. This could be interpreted as indicating that the ions separated in the solid anthracene by the radiation pass readily into the adjacent liquid, even though no ions are produced in the liquid itself by the same light.

Other substances dissolved in hexane were tested by Volmer and the volume ionization measured. The results are given in Table 8-4 together with Stark's relative values for the surface photoelectric effect of the solid substances. It is clear that a parallelism exists. No information is given as to the thresholds for these solutions, although it is implied that they are approximately the same for anthracene in hexane.

TABLE 8-4.—PHOTOCONDUCTING LIQUIDS

Substance	Conductivity of solution	Surface photoelectric effect of solute
Naphthalene	0	1.2
Phenol	0	2.2
Phenanthrene	6	8.8
Diphenylmethane	7	17.0
β-Phenol	10	10.6
Anthracene	20	12.5
α-Naphthylamine	40	15.0
Diphenylamine	50	17.0

It is known that the spectral region 4000A to 2300A is very effective in stimulating fluorescence in solutions of anthracene. Yet Volmer's investigations showed clearly that no genuine *volume* photoconductivity could be associated with it. The conclusion that fluorescence is not necessarily conditioned by a complete separation of an electron from its parent system has been confirmed by other investigators.[1]

Paraffin oil, between brass plates 2 mm apart, shows an increase in conductivity when illuminated by light from a quartz-mercury lamp, according to Szivessy and Schäfer.[2] As no precautions were taken to avoid illumination of the electrodes, it is not certain whether the observed currents are not partly, if not wholly, due to surface photoelectric effects at the electrodes. Curves are given by these authors showing the extremely slow rise and fall of the current after the light is

[1] P. PRINGSHEIM, "Fluorescenz und Phosphorescenz," p. 189 (Julius Springer, 1928).

[2] G. SZIVESSY and K. SCHÄFER, *Ann. d. Phys.*, **35**, 511 (1911).

turned on and off, and showing the current-potential relation approaching saturation. Timpanaro also found that ultra-violet light increased the conductivity of paraffin oil.[1]

Quite recently Eller has obtained very interesting results on the photoconductivity of a number of organic liquids.[2] The liquids were held by capillarity in layers 0.085 mm thick, between a quartz plate and a glass

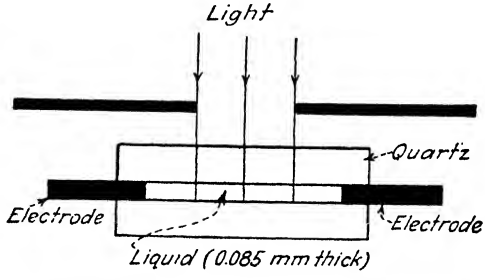


FIG. 8-64.—Arrangement for investigating photoconductivity of liquids.

plate as shown in Fig. 8-64. The electrodes were out of the path of the light. Currents were measured by an electrometer. The potential difference applied to the liquid was not mentioned; a diagram of the apparatus suggests that but one cell (1 to 2 volts) was used. Figure 8-65 is a typical current-time curve for paraffin oil. At A the illumination was begun. Evidently the resistance did not reach a steady (lower)

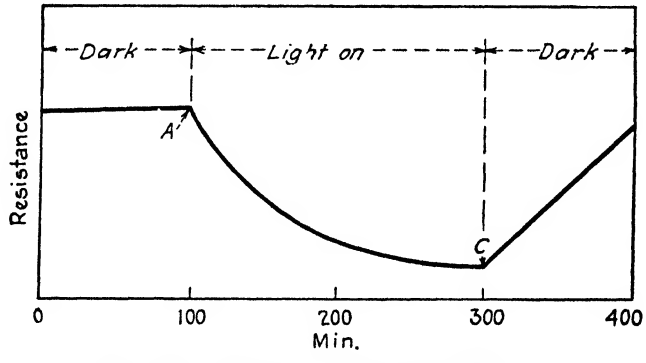


FIG. 8-65.—Photoconductivity of paraffin oil.

value until after about 2 hr. At C the light was turned off, after which the resistance increased linearly with the time. If n be the number of ions present per cubic centimeter, and α the coefficient of recombination, we know from the theory of ionization in gases that the rate of diminution of n, due to recombination, should be given by $dn/dt = -\alpha n^2$. Since the resistance r is inversely proportional to n, the equation can be changed to $dr/dt = \alpha$, which implies that the resistance increases linearly

[1] S. TIMPANARO, *Nuovo Cimento*, **24**, 203 (1922).

[2] W. H. ELLER, *Jour. Opt. Soc. Amer.*, **20**, 71 (1930).

with the time after the source of ionization has been removed. Since this is found to be the case experimentally, we may conclude that recombination between positive and negative ions is taking place according to this equation. The thresholds found for the liquids are given in the table. The absorption coefficients of these liquids remain very low as we

TABLE 8-5.—PHOTOCONDUCTING LIQUIDS

Substance	Absorption limit	Longest wave-length in Hg spectrum causing photoconductivity
Paraffin oil	2870A	2857A
n-Tetradecane	2810A	2804A
di-Isoamyldecane	2700A	2699A (2655A, 2654A, 2652A)
n-Decane	2660A	2655A, 2654A, 2652A
n-Octane	2365A	
iso-Octane	2365A	

Note: The octanes were rendered photoconducting by unresolved light from the mercury lamp: it was not possible, however, to determine the threshold by light from a monochromator.

go into the ultra-violet until, at a certain point, there is a characteristic, rapid, structureless increase in its value. (This is termed *end absorption;* other organic liquids, such as benzene, have a vibration structure in their ultra-violet absorption bands, *i.e.*, the bands have several maxima and minima.) Eller's experiments indicate that the wave-length of the threshold for the photoconductivity coincides with that of the absorption limit. (Benzene does not become photoconducting with the light from a mercury arc. As noted previously it does not have the characteristic "end absorption" of the other liquids.) Both the absorption limit and the photoconductivity threshold shift towards longer wave-lengths as one goes toward the higher members of the paraffin series. This is in accord with the earlier result of Volmer,[1] that pure hexane is not ionized by the light from a mercury lamp (shortest wave-length presumably 1850A).

It now appears certain that a real volume conductivity can be imparted to a number of organic liquids by ultra-violet radiation. A promising field is therefore opened up for investigation. Such questions as the following call for investigation: Do these liquids have sharply defined thresholds? (The absorption limit is not discontinuous.) Is there quantum equivalence between the number of charges released and the amount of light absorbed? Is there anything resembling the superposition of secondary currents on primary photoelectric currents as found by Gudden and Pohl for crystals? Can information as to the mechanism of the photoelectric process be obtained from a study of the mobilities of the ions? Is there a Hall effect as in crystals?

[1] M. VOLMER, *Ann. d. Phys.*, **40**, 775 (1913).

CHAPTER IX

PHOTOVOLTAIC EFFECTS

In 1839, Becquerel[1] discovered that, if one of two similar electrodes (platinum or silver, coated with a silver halide) immersed in dilute sulphuric acid were illuminated, a potential difference between them was produced. Rigollot[2] many years afterwards observed the same effect when he used certain fluorescent electrolytes, and also when he used electrodes covered with certain oxides and sulphides. Still later, Nichols and Merritt[3] observed, on illumination, an apparent change in the resistance of a cell containing certain fluorescent solutions, an effect which was traced down by Hodge[4] to a potential difference resulting from unsymmetrical illumination of the electrodes. We shall use the term photovoltaic effects to include phenomena associated with the production of an electromotive force in a cell consisting of two similar electrodes, separated by a suitable electrolyte or other substance, when the electrodes are unsymmetrically illuminated. (Some writers refer to these phenomena as Becquerel effects.) The success of the photoelectric viewpoint in its own field led some physicists, notably Goldmann, to regard photovoltaic effects as fundamentally photoelectric in character. While it seems possible to interpret certain selected results photoelectrically, there are many discordant results difficult to interpret on any view. In fact, it would be difficult to find a more discouraging assortment of conflicting experimental results than those which are classified under the title of photovoltaic effects. Most investigators reject the photoelectric interpretation altogether and regard the phenomena as entirely photochemical in character.

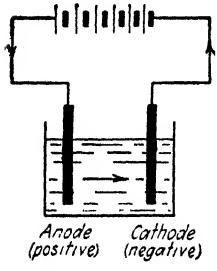


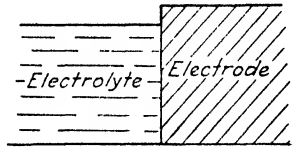
FIG. 9-1.—Illustrating terminology in photovoltaic effects; arrow indicates direction of current.

Before proceeding to a systematic discussion of the published results, it is desirable to explain the terminology to be used in this chapter, especially as different investigators use the same terms in various ways. If a current be driven by an outside source of e.m.f. through the cell (Fig. 9-1), the current *through* the electrolyte *leaves* the *anode*, which

[1] E. BECQUEREL, *Comptes Rend.*, **9**, 144, 561 (1839).
[2] H. RIGOLLOT, *Jour. d. Physique*, **6**, 520 (1897).
[3] E. L. NICHOLS and E. MERRITT, *Phys. Rev.*, **19**, 415 (1904).
[4] P. HODGE, *Phys. Rev.*, **28**, 25 (1908).

is the *positive* electrode. If the cell supplies the e.m.f. for the circuit (Fig. 9-2), the current *through* the electrolyte leaves the *anode*, which is now called the *negative* electrode. With but one exception (Goldmann), all investigators study cells without an externally applied e.m.f. and so the terminology of Fig. 9-2 is applicable.

The photovoltaic effect has been studied (1) in cells in which the electrodes are oxides, sulphides, or halides of certain metals and in which the electrolyte is a solution of an acid or an inorganic salt; (2) in cells in which the electrodes are pure metals dipping in inorganic electrolytes; (3) in cells in which we have pure metal electrodes dipping in a fluorescing solution; and, finally, (4) in cells consisting of



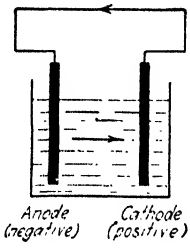


FIG. 9-2.—Illustrating terminology in photovoltaic effects; arrow indicates direction of current.

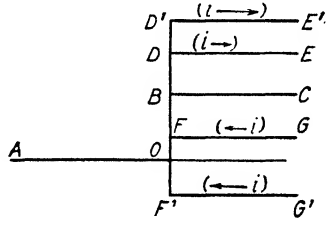


FIG. 9-3.—Potential distribution at electrolyte-electrode boundary.

two metals with a partial conductor such as selenium or molybdenite in between them. In case 2, the potential differences recorded seldom exceed 10 microvolts; in all the other cases, the potential differences observed run as high as 100 millivolts or more.

9-1. Compound Electrodes in Non-fluorescing Solutions.—Although almost all investigators have studied the e.m.f. developed within the cell itself when suitably illuminated, Goldmann[1] has made use of a circuit with an external battery. His results may be summarized as follows: Let $AOBC$ represent the potential distribution at an electrolyte-electrode interface when not illuminated (Fig. 9-3). If a current is driven through the cell, this potential distribution may be changed to $AODE$ or $AOD'E'$, or, if the current be reversed in direction, to $AOFG$ or $AOF'G'$. Thus, by adjusting the current flow, this potential difference may be kept at any desired value (within certain limits). If now the electrode-electrolyte boundary be illuminated, then, in general, it is found that an extra current must be supplied by the external battery to hold the potential

[1] A. GOLDMANN and J. BRODSKY, *Ann. d. Phys.*, **44**, 849 (1914).

distribution unchanged. On plotting δi as a function of the potential drop across the boundary Goldmann obtained the curve shown in Fig. 9-4. The similarity between this and the ordinary photoelectric voltage-current curves is evident and led him to conclude that the photovoltaic effect is photoelectric in its origin. Further support for this view was found in the fact that δi is independent of the thickness of the copper oxide film on the electrode and of the nature of the electrolyte. Furthermore, provided the electrolyte is kept well stirred, δi is nearly proportional to the intensity of the light.

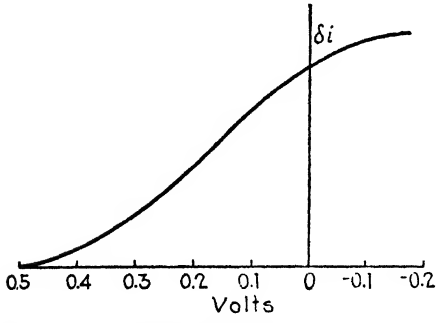


FIG. 9-4.—Current-voltage relation in a photovoltaic cell.

It is interesting to record that the magnitude of δi is of the order ten times that of the photoelectric currents in the alkali-metal cells, being about 10^{-5} amp/cm^2 for a 14-cp lamp at a distance of 75 cm.

Van Dijck[1] repeated Goldmann's experiments, but used monochromatic light instead of white light. His results are shown in Fig. 9-5. It is surprising that all the curves cut the axis at the same point, 0.4 volt; one would expect that the shorter the wave-length the higher would be the voltage value of the intercept. Evidently the photovoltaic effect cannot be regarded simply as a photoelectric effect at the electrode unaccompanied by any other phenomena.

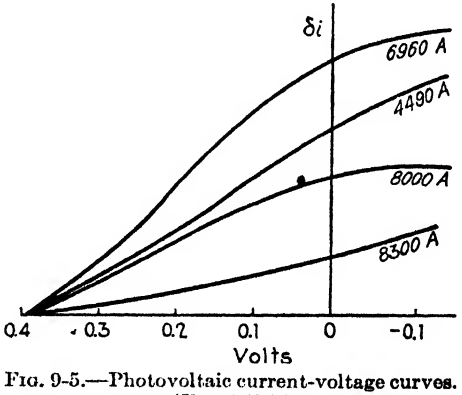


FIG. 9-5.—Photovoltaic current-voltage curves. (*Van Dijck.*)

On Goldmann's view, when one electrode in a simple photovoltaic cell is illuminated, the potential difference across the electrolyte-electrode interface builds up (or tends to build up, if the circuit be closed) to a value sufficient to stop the emission of the photoelectrons. Hence the illuminated electrode should always be a cathode, *i.e.*, it should become more positive (Fig. 9-2). But it has been found that in some cases, *e.g.*, silver halides on silver,[2,3,4,5] the illuminated electrode becomes

[1] W. J. VAN DIJCK, *Trans. Faraday Soc.*, **21**, 630 (1925).
[2] E. BECQUEREL, *Comptes Rend.*, **9**, 144, 561 (1839).
[3] G. M. MINCHIN, *Phil. Mag.*, **31**, 207 (1891).
[4] M. WILDERMAN, *Zeits. f. Phys. Chem.*, **59**, 553, 703 (1907).
[5] T. W. CASE, *Trans. Amer. Electrochem. Soc.*, **31**, 351 (1917).

the cathode, while in other cases[1,2] it becomes the anode, and frequently, during illumination, it may change from one to the other.[2]

Garrison,[3] using a 500-cp lamp at 25 cm records an e.m.f. of 0.3 volt in a cell with cuprous oxide electrodes in various electrolytes. The sign of the e.m.f. depended largely on the conditions; thus in many cells the illuminated electrode was initially a cathode, but with continued illumination it became an anode. Garrison believed that the light shifted the equilibrium constant of

$$Cu_2O \text{ (solid)} \leftrightarrows Cu_2O \text{ (dissolved)},$$

causing increased solubility which led to a change in the potential drop at the electrode boundary. Later he found that with thin coatings of

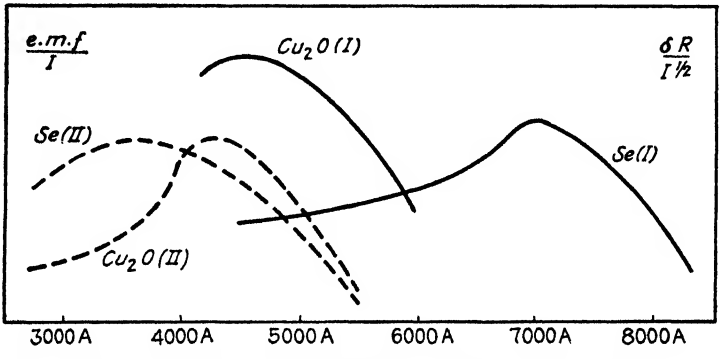


FIG. 9-6.—Photoconductivity and photovoltaic effects in Se and Cu_2O. (I) Photoconductivity $= \frac{\text{resistance change}}{(\text{light intensity})^{1/2}}$ (because $\delta R \propto I^{1/2}$). (II) Photovoltaic e.m.f. $= \frac{\text{change in e.m.f.}}{\text{light intensity}}$

silver iodide the electrode was always positive, while with thicker coatings it began as a negative electrode but became positive on continued illumination.[4] Miss Barton[5] measured the current produced by the e.m.f. developed in cells containing a pair of Cu_2O electrodes and a pair of selenium electrodes, water being the electrolyte in each case. With spectrally resolved light, she compared the photovoltaic e.m.f. and the photoconductivity (Fig. 9-6). While the curves are far from being superposable, there is a certain suggestive parallelism. There was, on the other hand, no connection to be found with the surface photoelectric effect for these substances, for the thresholds were 2500A (Cu_2O) and 2300A (Se).

[1] E. BECQUEREL, *Comptes Rend.*, **9**, 144, 561 (1839).
[2] G. M. MINCHIN, *Phil. Mag.*, **31**, 207 (1891).
[3] A. D. GARRISON, *Jour. Phys. Chem.*, **27**, 607 (1923); **28**, 279 (1924).
[4] A. D. GARRISON, *Jour. Phys. Chem.*, **28**, 337 (1924).
[5] V. P. BARTON, *Phys. Rev.*, **23**, 337 (1924).

From a systematic study of a large number of cells (electrodes, silver halides and cuprous oxide; electrolytes, a large variety of salt solutions) Tucker[1] gives the following rule for determining the direction of the e.m.f. developed in the cell. The illuminated electrode becomes a cathode (or anode) if the photosensitive surface is tending to become photochemically oxidized (or reduced) by the electrolyte. Deviations from this rule are attributed to local action on the surface of the electrode. He considers the phenomenon to be a purely photochemical one.

A partial return to the photoelectric viewpoint has been made recently by Winther.[2] He recognizes that Van Dijck's work makes it difficult to consider that the potential differences observed can arise immediately from the emission of photoelectrons from the electrode into the electrolyte. Since it is known that the materials used (cuprous oxide, silver halides) are photoconducting, he suggests that the change in conductivity induced by the light may be regarded as physically changing the adsorptive power of the material for ions, an effect which results in the appearance of a change in the potential. In his second paper, he finds that to maintain the potential difference in a copper oxide cell when one electrode is illuminated, oxygen has to be supplied continuously (Rigollot had found the same electrodes to become inactive after prolonged illumination, owing to reduction). The difference in oxygen concentration between the inner and outer layers of the copper oxide, when it is made conducting by light, is considered to form an oxygen concentration cell; hence the photovoltaic effect. Disagreement with some of Winther's views is expressed by Lifschitz and Hooghoudt.[3]

Iimori and Takebe[4] studied the photovoltaic effects with silver iodide electrodes. (The method of preparation was not stated, nor the electrolyte used.) They found that the potential of the illuminated electrode always became positive. Time lags of from a few seconds to several minutes were observed between the beginning of the illumination and the attainment of the steady value of the potential difference. The region 4000A to 5000A was most effective. These authors believe that light breaks up silver iodide into free silver and iodine, which form a solid solution in the silver iodide. Thus the concentration of free iodine is greater on the illuminated electrode than on the other; to this is attributed the potential difference. Sheppard[5] and his associates find that, with silver bromide electrodes, the illuminated electrode always acquires initially a negative potential, but later a larger positive potential

[1] C. W. Tucker, *Jour. Phys. Chem.*, **31**, 1357 (1927).

[2] C. Winther, *Zeits. f. Phys. Chem.*, **131**, 205 (1927); **145**, 81 (1929).

[3] I. Lifschitz and S. B. Hooghoudt, *Zeits. f. Phys. Chem.*, **141**, 52 (1929).

[4] S. Iimori and T. Takebe, *Sci. Papers, Inst. Phys. Chem. Research, Tokio*, **8**, 131 (1928).

[5] W. Vanselow and S. E. Sheppard, *Jour. Phys. Chem.*, **33**, 331 (1929); S. E. Sheppard, W. Vanselow, and V. C. Hall, *Jour. Phys. Chem.*, **33**, 1403 (1929).

takes its place. In some experiments the time during which the electrode was negative was so short that it was necessary to use an oscillograph to reveal its presence. It was suggested that at the start many of the electrons released photoelectrically in the silver bromide travel with the light into the silver, thus making it more negative than before. Later, the slowly moving bromine atoms diffuse to the silver surface and attack it and to this was attributed the final positive potential of the electrode.

9-2. Pure Metal Electrodes in Non-fluorescing Electrolytes.—Audubert[1] investigated the potential differences appearing when one of two strips of the same clean pure metal immersed in an electrolyte was illuminated. Heat rays were removed from the radiation by a suitable filter. The potential differences observed were of the order of 10 to 20 microvolts, and therefore were much smaller than those dealt with in the previous section. The nature of the electrolyte seemed to have no effect on the results. However, platinum, copper, and mercury electrodes always became anodes (*i.e.*, as though they emitted electrons into the electrolyte), while silver and gold became cathodes. No explicit statement is made as to the effect of varying the light intensity. Audubert's interpretation of his results as pointing to a photoelectric origin of the potential differences was criticized by Athanasiu[2] on the ground that a cell containing two identical metals dipping into an electrolyte was very sensitive to temperature differences. Thus a difference of 1°C between the electrodes in a Zn-$ZnSO_4$-Zn cell gives 800 microvolts. This suggests that Audubert's effects were due merely to the small heating effect of the radiation used. In support of a purely chemical viewpoint, Athanasiu[3] shows that the addition of OH^- ions produces a diminution in the positive photovoltaic potential of the electrode, while the addition of H^+ ions increases it. On the other hand, Audubert[4] emphasizes the fact that the change in potential follows the change in light intensity without lag. This is inconsistent with a thermoelectric origin. The instantaneity of the effect is observed only when the liquid is not acted upon by the light. When the electrolyte is sensitive to radiation, the potential differences are much larger and take a considerable time (20 to 100 min) to attain full values.[5,6] Such an electrolyte is ferric chloride, in which the absorption of a quantum of frequency $h\nu$ is believed to convert trivalent ions into divalent ions. The change in the nature of some of the ions in the neighborhood of one

[1] R. Audubert, *Comptes Rend.*, **177**, 818, 1110 (1923).

[2] G. Athanasiu, *Comptes Rend.*, **178**, 386, 561 (1924).

[3] G. Athanasiu, *Comptes Rend.*, **188**, 786 (1929).

[4] R. Audubert, *Jour. d. Physique*, **6**, 313 (1925); *Jour. d. Chimie Phys.*, **24**, 357 (1927).

[5] S. Schlivitch, *Comptes Rend.*, **182**, 891 (1926).

[6] S. Iimori, *Sci. Papers, Inst. Phys. Chem. Research, Tokio, Supplement*, **8**, 2 (1928).

electrode is sufficient to account for a change in potential difference. It has been found that platinum electrodes, when illuminated, become more negative in some solutions (*e.g.*, $K_2Cr_2O_7$, $[NH_4]_2Cr_2O_7$, $NaNO_3$, KFeCN) and more positive in others (KN_2CN, KPbCN).[1,2] Time lag effects are considerable (see Fig. 9-7) but are apparently independent of the intensity of the light.

Grignard compounds are certain organo-magnesium halides which give out a faint luminosity under certain conditions. Dufford and Hammond[3] found that illuminating one electrode in a cell containing these compounds produced an e.m.f. between 0.01 and 0.001 volt (1000-watt lamp: distance not stated). The diagrams indicate that the illuminated electrode becomes more positive. When X-rays were used instead of light, a potential up to as much as 0.8 volt was developed.

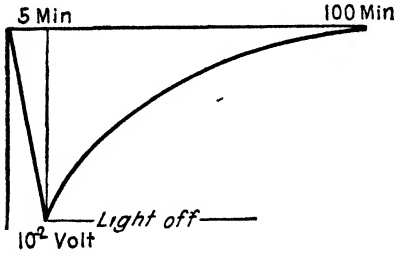


FIG. 9-7.—Photovoltaic e.m.f. for Pt electrodes in $K_2Cr_2O_7$.

9-3. Fluorescent Electrolytes.—Goldmann[4] made an extensive investigation of the effect of illuminating one electrode in a cell containing a fluorescent substance in solution. It was convenient to use semitransparent platinum films on the inside of the cells as electrodes and to pass the light in through one electrode. The procedure he adopted was very similar to that described in Sec. **9-1**, and the results obtained were of the same general character. The photoelectric current was found to be proportional to the intensity of the light and to be independent (within wide limits) of the resistance in the external circuit. The latter result led him to the view that a given quantity of light separates a corresponding number of charges at the electrode and hence the current is independent of the external resistance in the circuit. On open circuit, potential differences of the order of 0.25 volt were obtained. Thompson[5] found that the magnitude of the current obtained when two electrodes were dipped into rhodamine BX in alcohol, and one was illuminated, depended largely on the nature of the electrodes. Finite currents were obtained only with Pb, Ag, CuO, and Au electrodes.

By investigating photovoltaic effects in very dilute fluorescent solutions, Grumbach[6] was able to distinguish between two distinct effects.

[1] S. SCHLIVITCH, *Comptes Rend.*, **182**, 891 (1926).

[2] S. IIMORI, *Sci. Papers, Inst. Phys. Chem. Research, Tokio, Supplement*, **8**, 2 (1928).

[3] R. T. DUFFORD and H. E. HAMMOND, *Phys. Rev.*, **33**, 124 (1929); H. E. HAMMOND, *Phys. Rev.*, **35**, 998 (1930).

[4] A. GOLDMANN, *Ann. d. Phys.*, **27**, 449 (1908).

[5] G. E. THOMPSON, *Phys. Rev.*, **5**, 43 (1915).

[6] A. GRUMBACH, *Comptes Rend.*, **176**, 88, 395 (1923).

When the electrode itself is illuminated, its potential E_s becomes more positive, increases at a finite rate to a maximum, then decreases, and finally changes sign. If the liquid close to one electrode be illuminated, while the electrode itself is in the dark, then the electrode acquires a negative potential E_v from the start. E_v arises from the fact that light changes the liquid in the neighborhood of one electrode and so we have a kind of concentration cell. Murdock[1] confirmed the existence of E_v by pre-illuminating the fluorescent liquid (3 per cent rhodamine B in alcohol) before it passed the electrode. He was uncertain whether E_s existed in his experiments. Using improved methods, Lowry could find no evidence at all for the existence of E_s.[2] Stirring the liquid decreased the amount of the current resulting from illumination, a result to be expected since anything tending to equalize the condition of the liquid at each electrode would diminish the potential difference E_v arising from non-uniform concentration.[3] Rule found that the sign of the potential difference was reversed when eosin was substituted for fluorescein.[4] Grumbach went farther and showed that the signs of both E_s and E_v could be changed by suitable modifications of the electrolyte.[5] Both Rule[6] and Russell[7] carried out experiments in which they showed that the magnitude of the potential difference was closely related to the diffusion processes occurring in the cells. Thus Rule, using a cell in which diffusion from the vicinity of one electrode to the other was prevented by limiting the communicating tube to a narrow capillary, found the potential to build up with the time of illumination and with the light intensity in a definite manner. These results were accounted for by Ghosh,[8] who supposed that light changes a molecule of the fluorescent substances into an unstable molecule B. When two B molecules collide they form a third molecule. On the assumption that the potential difference between the electrodes arises from the presence of B molecules in the immediate vicinity of one of them, he applied Nernst's theory of concentration cells and deduced that the potential difference varies with the time in the way it did in Rule's experiments. He also showed that the maximum potential difference obtained varies as the square root of the light intensity, which was also in satisfactory accord with Rule's results. Russell found, contrary to Goldmann, that the photoelectric potential is not independent of the intensity of the light, and moreover

[1] C. C. Murdock, *Proc. Nat. Acad. Sci.*, **12**, 504 (1921).
[2] W. N. Lowry, *Phys. Rev.*, **35**, 1270 (1930).
[3] C. C. and D. W. Murdock, *Trans. Faraday Soc.*, **23**, 591 (1927).
[4] W. Rule, *Phil. Mag.*, **1**, 532 (1926).
[5] A. Grumbach, *Comptes Rend.*, **184**, 169 (1927).
[6] W. Rule, *Proc. Nat. Acad. Sci.*, **14**, 272 (1928).
[7] H. W. Russell, *Phys. Rev.*, **32**, 667 (1928).
[8] J. C. Ghosh, *Zeits. f. Phys. Chem.*, **3**, 419 (1929).

it is less with blue light than with yellow light, a result hardly to be expected photoelectrically.

9-4. Photovoltaic Effects with Partial Conductors.—In 1876, Adams and Day[1] found that if a selenium rod provided with platinum-wire electrodes were connected in a circuit without a battery, then a current was obtained on illuminating one junction. In general, the illuminated junction was at a negative potential with respect to the other, although occasionally the polarity was reversed.

Similar effects with selenium have been found by other observers,[2,3,4] using various types of electrodes. Potential differences as high as 0.12 volt were recorded with sunlight.[2] When one electrode was illuminated, it became negative.[2,3] Some investigators do not mention the polarity developed. The maximum effect was found to be at 4900A, and the photo e.m.f. was nearly proportional to the intensity of the light.[4] Kennard, Dieterich, and Moon[5] found that the contact difference of potential between a selenium surface and a near-by metal surface changes by about 0.1 volt when illuminated, and in such a direction as to make the surface of the selenium more negative than before. (When connected so as to form a circuit, the direction of the e.m.f. driving the current was consistent as to sign, although exceedingly small.) Holmes[6] found that the thermoelectric power of gray crystalline selenium, mounted on glass between nickel electrodes, is decreased 5 per cent when the selenium between the electrodes is illuminated, the conductivity being simultaneously increased five-fold. Later Holmes and Walbridge[7] discovered that while the photo e.m.f. produced by illuminating a single crystal of Se at the electrode boundary increased more slowly than the illumination and finally approached a maximum, the associated current increased steadily with the illumination. A current of 5.5×10^{-6} amp was obtained with an illumination of 4.4 lumens/cm^2.

Coblentz[8] found that when molybdenite crystals were connected in a circuit, without an external battery, illumination caused the appearance of an e.m.f. A point-by-point exploration of the specimen showed that the source of the e.m.f. was located at tiny spots distributed irregularly over the surface of the crystal. Occasionally a change from one spot to an adjacent spot would reverse the sign of the e.m.f. The photovoltaic properties of the crystal could not be correlated with its photoconduc-

[1] W. G. Adams and R. E. Day, *Proc. Roy. Soc.*, **25**, 113 (1876).

[2] W. Uljanin, *Ann. d. Phys.*, **34**, 241 (1888).

[3] E. Merritt, *Phys. Rev.*, **23**, 555 (1924).

[4] R. L. Hanson, *Jour. Opt. Soc. Amer.*, **18**, 370 (1929).

[5] E. H. Kennard and C. Moon, *Phys. Rev.*, **21**, 373 (1923); E. H. Kennard and E. O. Dieterich, *Phys. Rev.*, **9**, 58 (1917).

[6] R. M. Holmes, *Phys. Rev.*, **25**, 826 (1925).

[7] R. M. Holmes and N. L. Walbridge, *Phys. Rev.*, **33**, 281 (1929).

[8] W. W. Coblentz, *U. S. Bur. Standards, Sci. Paper* 486, p. 375 (1924).

tivity. Because of the fact that the currents produced in a circuit containing a selected flake of molybdenite were much greater than those produced by a thermocouple illuminated by the same feeble light, Coblentz[1] suggested the use of molybdenite for measuring feeble radiations. However, the lack of proportionality to light intensity and the variation in different parts of the spectrum would be a serious drawback.

Argentite[2,3,4] and acanthite[3] show photovoltaic effects when one of the contacts with them is illuminated. The polarity developed is not recorded. Mere thermoelectric effects were ruled out by obvious tests. For argentite the photovoltaic effect is most marked at 10,000A.[3] Destroying the crystal structure (*e.g.*, by hammering or filing) causes the photovoltaic effect to disappear.[4] This suggests a close connection with the phenomenon of photoconductivity. Schneider[4] found that the e.m.f. could be produced not only by illuminating the electrode-argentite boundary, but also by illuminating certain sensitive spots distributed here and there over the surface of the argentite (*cf.* Coblentz's results for molybdenite[1]).

9-5. Cuprous Oxide Cells.—A new type of photocell, which has many desirable characteristics, has been developed recently by Lange.[5] It

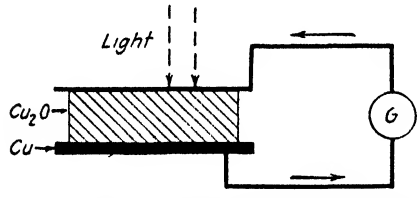


FIG. 9-8.—Lange's photocell. Arrows indicate direction of flow of electrons through galvanometer.

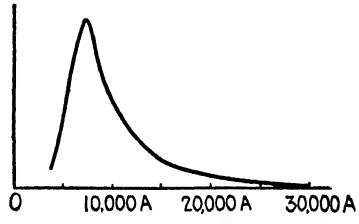


FIG. 9-9.—Spectral distribution curve for Lange's cell.

consists simply of a thin layer of cuprous oxide (Cu_2O) between two metal electrodes. While ordinary vacuum or gas-filled photoelectric cells require an external source of potential to operate them, this new photocell requires none. In a sense it provides its own e.m.f. to drive the current around a circuit, and so it is considered as a photovoltaic effect.

Grondahl[6] appears to have been the first to discover that light has some effect on a Cu_2O-on-Cu rectifier, and saw how it could be used as a photocell. Lange found the same effect and devised a special arrangement of the elements in the rectifier to form a photocell of very great

[1] W. W. COBLENTZ, *Phys. Rev.*, **29**, 615 (1927).
[2] H. H. SHELDON and P. H. GEIGER, *Phys. Rev.*, **19**, 389 (1922).
[3] P. H. GEIGER, *Phys. Rev.*, **22**, 461 (1923).
[4] W. A. SCHNEIDER, *Phys. Rev.*, **31**, 82 (1928).
[5] B. LANGE, *Phys. Zeits.*, **31**, 139 (1930); **31**, 964 (1930).
[6] L. O. GRONDAHL, *Science*, **36**, 306 (1926); *Jour. Amer. Inst. Elec. Eng.*, **46**, 215 (1927).

sensitivity. His cell consists of a base plate of Cu, then a thin layer of Cu_2O (probably $< 10\mu$ thick), and finally a semitransparent film of metal (Fig. 9-8). When this is connected in series with a galvanometer and illuminated, a current flows without the assistance of any battery. The current is strictly proportional to the light intensity and follows changes in it without appreciable lag. Figure 9-9 shows the response of the cell to an equal energy spectrum. The threshold is at 66,000A and the maximum yield occurs near 8000A. This spectral distribution curve at once rules out a thermoelectric explanation of the effect. The yield of the cell is very high, the effect being approximately ten times as great as that of a good alkali cell in a vacuum. (Lange does not state whether these figures refer to incident energy or to absorbed energy, or whether they refer to the whole spectrum, or to that part of it on the short wavelength side of the threshold, or to that part of it in the immediate vicinity of the maximum sensitivity. He gives the yield of an alkali cell as 2.05 coul/cal, which is probably a misprint, for the best yields hitherto obtained are of the order of 3×10^{-2} coul/cal.) In one of his articles he states that a cell (presumably not more than a few square centimeters in area) gave a current of 10^{-4} to 10^{-5} amp when illuminated by 1 lumen/cm^2. A cell of area 50 cm^2, when illuminated by sunlight, generates sufficient current to drive a small motor! Graffunder[1] found that a certain Cu_2O-on-Cu rectifier, when illuminated by a 60-watt lamp at 10 cm, gave a current of 2×10^{-5} amp.[2]

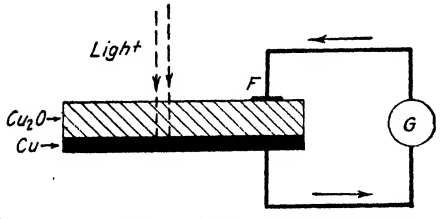


FIG. 9-10.—Arrows indicate direction of electron current through galvanometer.

Systematic investigations of the properties of these cells have been carried out by Schottky[3] and by Auwers and Kerschbaum.[4] The following account is a summary of their results.[5] A useful form of cell for testing certain theories of its action is shown in Fig. 9-10. The Cu_2O

[1] W. GRAFFUNDER, *Phys. Zeits.*, **31**, 375 (1930).

[2] It should be recorded that a photocell consisting of a single Se crystal with semitransparent Pt electrodes when operated in the same way as Lange's cell gave a current of about 5×10^{-6} amp with light whose intensity was 4 lumens/cm^2 (R. M. Holmes and N. L. Walbridge, *Phys. Rev.*, **33**, 281 [1929]).

[3] W. SCHOTTKY, *Phys. Zeits.*, **31**, 913 (1930).

[4] Q. v. AUWERS and H. KERSCHBAUM, *Ann. d. Phys.*, **7**, 129 (1930).

[5] It is evident from the various papers describing the new cell that its yield depends greatly on how it is made, yet nowhere does one find a clear statement giving the best thickness of Cu_2O to use, how it should be prepared, and how the Cu_2O and the metal electrodes should be assembled. Commercial reasons no doubt account for this reticence. It appears, however, that the Cu_2O is formed directly on the Cu base plate by heating in air for a long time at a temperature just below its melting point.

is formed on the Cu base plate by heating. The auxiliary electrode F may be a piece of metal pressing on the top surface, or a film of sputtered or evaporated metal. Such a cell is a rectifier in which the current is allowed to pass in one direction but is *blocked* in the other direction. Electrons are *allowed* to pass directly *from* the Cu *to* the Cu_2O, but the passage of electrons *from* the Cu_2O to the Cu is *blocked.* (It is to be understood, of course, that these terms are relative; the current is not completely stopped in the blocked direction.) Now, when light is allowed to fall on the cell, the photocurrent flows in that direction which blocks the current when the cell is used as a rectifier—an unexpected result.

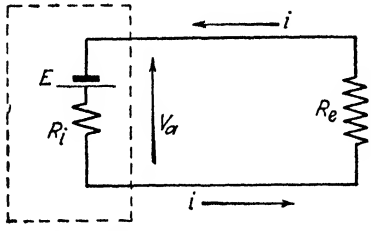


FIG. 9-11.—Equivalent potential source. V_a = potential difference across external resistance. Arrows (i) indicate direction of flow of electrons.

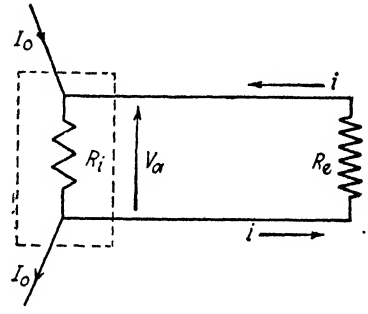


FIG. 9-12.—Equivalent current source. V_a = potential difference across R_e. Arrows (i) indicate direction of electron flow.

(This is shown in Fig. 9-15, the photocurrent which we are now considering being OE.) The results are consistent with the view that photoelectrons are released at the boundary between the Cu_2O and the Cu, and travel from the former to the latter. (An equivalent view is that photoelectrons are released in the materials on each side of the boundary, but that more move from the Cu_2O to the Cu than in the opposite direction.)

The fundamental effect at the boundary may be either the development of an e.m.f. which is proportional to the light intensity, or the passage of a photoelectric current which is proportional to the light intensity. That the latter is the correct assumption was established by Auwers and Kerschbaum.

When the light intensity is held constant, the boundary may be considered as equivalent *either* to a cell of constant e.m.f. E and having an internal resistance R_i, *or* to a device providing a constant current I_0 and having an internal resistance R_i (Figs. 9-11, 9-12). Since we are dealing with a rectifier, we may assume that R_i is *not* independent of the current through, or potential difference across, the boundary; hence we may write $R_i = R_0 + R_0'I + \cdots$, or $1/R_i = G_0 + G_0'E + \cdots$ The values of the open-circuit potential drop across the circuit ($R_e = \infty$) and those of the short-circuit current ($R_e = 0$) depend on which assumption we take, and are as follows:

I	II
E.M.F. FUNDAMENTAL	CURRENT FUNDAMENTAL
(Fig. 9-11)	(Fig. 9-12)
Open-circuit potential drop ($R_e = \infty$)	
$V_a = E$	$V_a = R_iI_0 = R_0I_0 + R_0'I_0^2 + \cdots$
Short-circuit current ($R_e = 0$)	
$i = E/R_i$	$i = I_0$
$= G_0E + G_0'E^2 + \cdots$	

On varying the intensity of the light incident on the photocell, the results shown in Fig. 9-13 were obtained. It is therefore clear that the correct representation to take for the effect at the boundary is that the fundamental effect is the production of a photoelectric current, and not an e.m.f., which is proportional to the light intensity. Whereas in an ordinary voltaic cell, the e.m.f. is fundamental and the current is derived, here the reverse is the case. On open circuit the primary photoelectric current builds up a potential difference across the boundary, which, because of its finite resistance, allows a current of electrons to leak back. Since the resistance is not a constant, the potential difference built up is not proportional to the current. Because the resistance of the rectifier in the "allowed" direction (Cu to Cu_2O) diminishes as the potential across the boundary increases, it is easy to account for the type of curvature of curve 1 in Fig. 9-13. On short-circuiting the cell through a galvanometer, however, no potential difference is built up and the measured current is equal to the primary photoelectric current. (One should qualify this statement with the remark that this applies only to cases in which the effect to be described in the next paragraph is negligible.)

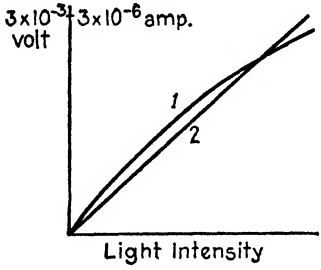


FIG. 9-13.—Dependence of e.m.f. and current on light intensity. 1. Open-circuit e.m.f. 2. Short-circuit current.

Schottky,[1] and Auwers and Kerschbaum,[2] found that the short-circuit current diminished as the distance of the illuminated strip from the auxiliary electrode F was increased (Fig. 9-10). The form of the curve obtained was accounted for quantitatively by a model in which the Cu_2O was replaced by an infinite number of resistances in series, while the Cu_2O-Cu boundary was replaced by an infinite number of resistances in parallel, as shown diagrammatically in Fig. 9-14. The leakage of the electron current back through the boundary is responsible for the diminution of the measured current. For practical applications, of course, this effect should be as small as possible. The dependence of the current on the position of the illuminated spot may be diminished by making the cell in such a way that the Cu_2O layer has a low resistance, while the Cu_2O-Cu boundary has a high resistance. This evidently can be realized sometimes, for in a photocell examined by Graffunder[3] it

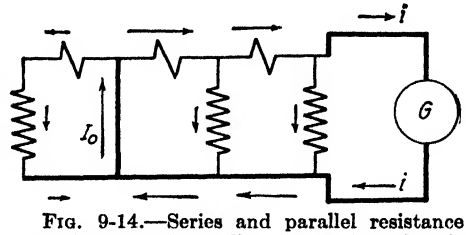


FIG. 9-14.—Series and parallel resistance equivalent of photocell. I_0 = photoelectric current produced by the light. i = measured photocurrent.

[1] W. SCHOTTKY, *Phys. Zeits.*, **31**, 913 (1930).
[2] O. v. AUWERS and H. KERSCHBAUM, *Ann. d. Phys.*, **7**, 129 (1930).
[3] W. GRAFFUNDER, *Phys. Zeits.*, **31**, 375 (1930).

appears that the Cu_2O resistance was negligible in comparison with the Cu_2O-Cu resistance, since the measured current was practically independent of the position of the spot of light. When the light actually passes through the auxiliary electrode, as in Lange's cell (Fig. 9-8), this effect is negligible.

Current-voltage curves for the Cu_2O-Cu cells in the dark and in the light are shown in Fig. 9-15. *OE* measures the primary photoelectric current. As the applied voltage is increased, the difference between the light and dark currents diminishes. This is due in part to more and more photoelectrons leaking back through the boundary. In addition, light increases the photoconductivity of the Cu_2O layer. This probably helps to account for the crossing over of the two curves at a certain value of the voltage.

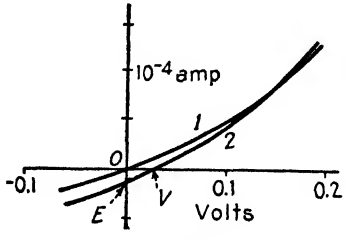


FIG. 9-15.—Current voltage characteristics of a Cu_2O-Cu cell. 1. In the dark. 2. When illuminated. *OE*, short-circuit current. *OV*, open-circuit voltage.

Lange's cell (Fig. 9-8) has a semitransparent metal film for its "front" electrode. His first interpretation of his results was that photoelectrons were released from the metal film to the Cu_2O. In view of the work of Schottky and that of Auwers and Kerschbaum, and of Lange's later work, it appears certain that the photoelectrons travel *from* the Cu_2O *to* the Cu and consequently in Lange's cell the effect occurs at the *back* boundary. This raises the question why should the effect not appear equally well at the *front* boundary as at the *back* boundary. The answer is that effects at both boundaries can be obtained. Thus Schottky constructed a photocell by sputtering metal on to the front surface of a layer of Cu_2O at the back of which was a suitable electrode. Conditions were so chosen that, in this cell, the front boundary of the Cu_2O had a large rectifying action, while the back boundary had very little. Such a cell when illuminated gives, as one would expect, a current in the opposite direction to that in Lange's cell (Fig. 9-8). The maximum sensitivity of a front-boundary cell is found to be in the green, while that for a back-boundary cell occurs in the infra-red. The difference is due to the fact that the Cu_2O acts as a red filter.

No details are given as to how the rectifying power of a boundary can be altered at will. (There are no doubt good reasons—from a commercial standpoint—for not revealing the manner in which good cells are made.) We may infer from a paper published by Vogt[1] on a related subject that it depends not only on the materials used for the rectifier but also on the way in which they are put together. Thus he states that a contact made by pressing metallic Cu on to Cu_2O has not nearly so high a boundary resistance (and therefore presumably not nearly so large a rectifying effect), as when the Cu_2O is formed directly on the Cu by heating. However, Vogt believes that CuO in contact with Cu, or with Cu_2O, is necessary for rectification, a view which differs from that of the other investigators referred to in this section.

[1] W. VOGT, *Ann. d. Phys.*, **7**, 183 (1930).

Teichmann[1] finds that the yield of a Lange cell increases by about 150 per cent as the temperature is lowered to about −100°C and then drops rapidly, becoming zero at −130°C. He gives no explanation for this. We suggest that the disappearance of the current is connected with the fact that the resistance of a mass of small crystals welded together, such as the Cu_2O layer is, becomes almost infinite at low temperatures. This, of course, leaves the change of resistance above −130°C unaccounted for; an entirely different explanation is probably needed for this effect.

The behavior of a Cu_2O-Cu photocell appears to be satisfactorily accounted for on the view that more photoelectrons cross the boundary from the Cu_2O to the Cu than cross it in the opposite direction. (It is conceivable that no photoelectrons at all cross from the Cu side to the Cu_2O side.) This is little more than a description of the facts, however. Is the photoelectric effect here due to a much higher yield of photoelectrons on the Cu_2O side of the boundary than on the Cu side? If not, what is the nature of the effect at the boundary which simulates the action of a valve allowing the photoelectrons to travel one way but favoring the transmission of electrons under an applied field in the opposite direction? The apparent conflict of these two effects makes it appear difficult at first sight to explain them in terms of a simple potential jump at the boundary. Yet the close association of the photoelectric effect in these cells with their rectifying action makes it highly probable that when we have a satisfactory theory of rectification we shall also have an explanation of the transfer of photoelectrons across the boundary. It is possible that considerations similar to those proposed by Frenkel[2] to account for certain characteristics of contact resistance may explain the properties of the cuprous oxide cells.[3]

9-6. Summary.—It is clear from a consideration of the results obtained in the foregoing sections that the evidence as to the origin of certain photovoltaic effects is conflicting. The majority of investigators in this field appear to believe that the photovoltaic effect is fundamentally photochemical in its nature and not photoelectrical. If one asks for a clear-cut criterion for discriminating between a photochemical and a photoelectric effect, it is not easy to give one which is

[1] H. Teichmann, *Phys. Zeits.*, **31**, 216 (1931); *Zeits. f. Phys.*, **67**, 192 (1931).

[2] J. Frenkel, *Phys. Rev.*, **36**, 1604 (1930).

[3] Since this section was written, the following papers have appeared: "The Photoelectric Effect in a Cu_2O-Cu Rectifier" by E. Perucca and R. Deaglio (*Ann. d. Phys.*, **10**, 257 [1931]) and by O. v. Auwers and H. Kerschbaum (*Ann. d. Phys.*, **10**, 262 [1931]); "Remarks on Photoelectric Cells and the Formation of Photoelectrons" by S. E. Sheppard and W. Vanselow (*Phys. Zeits.*, **32**, 454 [1931]); "On the Photoelectromotive Force in Cu_2O-Cu Cells" by H. Dember (*Phys. Zeits.*, **32**, 554 [1931]); "Is the Effect in a Rectifier Photocell a Hallwachs Effect?" by E. Perucca and R. Deaglio (*Zeits. f. Phys.*, **72**, 102 [1931]).

thoroughly logical and also consistent with current usage. In the photoelectric effect the fundamental thing is the separation of an electron from an atom as the result of the absorption of a quantum, while in a photochemical effect what happens is the raising of the energy state of a molecule to another level, resulting in a modification of its chemical properties. (The changing of the valency of an ion in solution due to illumination would according to this criterion be a photoelectric effect; it happens that such processes, however, are classed as photochemical.)

In favor of the photoelectric viewpoint, we have Goldmann's current-potential curves, the instantaneity of some of Audubert's effects and a certain correspondence between the effects with electrodes of silver halides and oxidized copper, and the photoconductivity known to exist in these compounds. It will be remembered that such electrodes gave relatively large photovoltaic effects. The photovoltaic effects arising from illumination of the electrolytes, *e.g.*, the solutions of fluorescent materials, are probably of photochemical origin.

Much more work needs to be done to unravel the nature of the photovoltaic effect; it appears that the methods used in studying the potential differences in photovoltaic cells have been disappointing in that they have revealed little as to the fundamental nature of this effect.

CHAPTER X

PHOTOELECTRIC EFFECTS IN NON-METALLIC SUBSTANCES

Although the term surface photoelectric effect usually implies a photoelectric effect in metals, its existence in certain non-metallic substances, both solid and liquid, conducting and non-conducting, has been demonstrated in a number of investigations. In point of significance and precision of results, and in correlation with theory, the study of the surface photoelectric effect in non-metallic substances has, however, made relatively little progress. It is frequently asserted that the difference between insulators and metals is that the electrons are *bound* in one case, and *free* in the other. The existence of a photoelectric effect in insulators indicates that it is not necessarily conditioned by the presence of free electrons. The phenomenon of photoconductivity, so ably unraveled by Gudden and Pohl, shows that many insulating crystals are made conducting by illumination with relatively long wave-length light. The threshold for the surface photoelectric effect for such crystals is either much farther in the ultra-violet or else cannot be detected at all within the range of wave-lengths usually available. Consequently more energy is necessary to release a bound electron within an insulator and to carry it through the surface than merely to set it free inside. Hence the surface of an insulator resembles that of a metal in that each has a work function.

Conducting, non-metallic substances may be divided into two classes according as to whether the conductivity is electronic or ionic. It is possible that the photoelectric characteristics would be different for the two classes, but the single investigation which has been made with this distinction in mind does not reveal any clear-cut difference. The absorption of light in non-metallic substances is as a rule far less than in metals. In such substances a small photoelectric yield is to be expected since only that light which is absorbed in the surface layer is effective in producing the photoelectrons which escape.

Several factors have retarded the photoelectric investigations in non-metallic substances. As a rule, when a photoelectric effect is detectable the threshold is frequently so far in the ultra-violet that the range of wave-lengths over which the effect can be studied is severely limited. If the substance be an insulator, the escape of photoelectrons results in the building up of a positive charge on the surface, and the actual field acting on the photoelectrons steadily changes and is hard to determine.

It must be admitted that the technique of investigating photoelectric effects in non-metallic substances has far to go before it is equal to that

associated with the effect in metals. Although one or two investigations have been carried out using modern high-vacuum technique to secure thorough outgassing, most investigations have been conducted in air at atmospheric pressure. Spectral-distribution curves are almost nonexistent. Thresholds have been determined in relatively few cases. Little is known about the energy distribution of photoelectrons from insulators. Finally, while the possibility of the occurrence of photochemical changes during an experiment has been recognized, it has seldom been taken into account.

10-1. Experimental Methods.—The photoelectric properties of nonmetallic substances are frequently investigated in an apparatus of which the essential features are as shown in Fig. 10-1. The substance is laid on the lower plate P. If it is photoelectrically active under proper illumination, an accelerating potential applied to the grid G allows a photoelectric current to flow, which is measured by M, usually an electrometer. When the substance is a conductor, even though it may possess only a very slight conductivity, it takes up the potential of the supporting plate P, and thus the field between G and the surface of Q is clearly defined. However, when the substance is a good insulator, certain new experimental problems arise. As the surface of Q loses electrons, an increasing positive charge is left behind, which tends to annul the field between G and Q. This, in turn, reduces the photoelectric current—especially when gas is present—and has been taken as evidence for "fatigue," a term which should not be used for a decrease in a photoelectric current arising merely from a change in the effective accelerating potential. Some investigators have worked with the smallest measurable currents to diminish as far as possible the effect of the growing positive charge on the surface. Others have discharged the surfaces between observations by warming the substance (to induce a slight conductivity) or by admitting moist air. One may question whether the observed photoelectric effect in such cases is really that characteristic of the pure substance; it is much more likely to be that characteristic only of the surface as modified in any particular experiment.

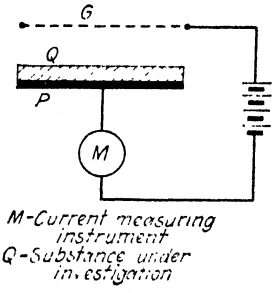


FIG. 10-1.—Apparatus for investigating surface photoelectric effects in insulators.

Attention should be called to the fact that the observed current may also include an effect due to photoconductivity induced within the layer of insulating material—a volume photoelectric effect—in addition to the surface photoelectric effect. Pauli[1] found that when anthracene (in an apparatus similar to that outlined in Fig. 10-1) was illuminated by

[1] W. E. PAULI, *Ann. d. Phys.*, **40**, 686 (1913).

ultra-violet light, the results shown in Fig. 10-2 were obtained. The ordinates in curve 1, taken with the grid positive, are higher than those in curve 2, taken with the grid negative, because the electrons released from the surface are drawn across to the grid in the first case but are turned back in the second case. The part of the observed current due to the photoconductivity induced *within* the insulating layer is, of course, independent of the direction of the field.[1] It falls off rapidly after the illumination has been turned on and disappears when the polarization set up by the displacement of the charges annuls the applied field within the insulator. (The phenomenon of photoconductivity is discussed fully in Chapter VIII.) When this stage has been reached, a current is

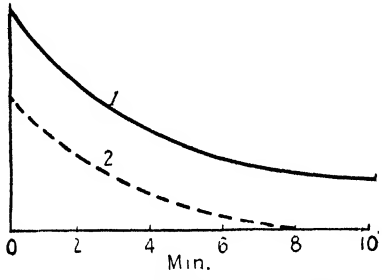


FIG. 10-2.—Photoelectric effect in anthracene (with ultra-violet light). 1. G at + potential. 2. G at − potential.

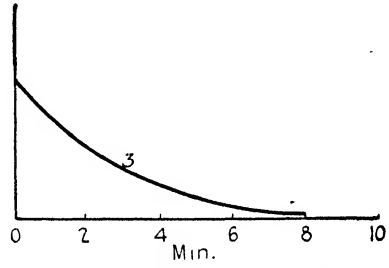


FIG. 10-3.—Photoelectric effect in anthracene ($\lambda > 4800$A). 3. Curve for G either positive or negative.

observed only when G is positive and is then due entirely to the surface photoelectric effect. (Later on, this too may disappear when the surface has charged up sufficiently to annul the applied field between it and G.) Light of longer wave-length is incapable of producing a surface photoelectric effect, although it may still be able to produce photoconductivity (Fig. 10-3). The natural explanation for this is that it takes a finite amount of energy to pull electrons through the surface after they have been set free inside the insulator.

A very ingenious method of investigating photoelectric effects of non-metallic substances originated with Millikan's discovery[2] that the charge on the droplet in his famous experiment to determine e could be changed by exposing the droplet to suitable ultra-violet light. A drop or particle is introduced between the plates of a condenser arranged in a horizontal plane. If the drop or particle be initially charged. it is possible to hold it at rest by an electric field which just counterbalances the force of gravity. Motion immediately follows an *alteration* in its charge, such as may arise when it is illuminated, and thereby loses photo-

[1] This effect induced by light within the material is occasionally called the "actinodielectric effect."

[2] R. A. MILLIKAN, "The Electron," p. 135 (The University of Chicago Press, 1924).

electrons. The loss of a single electron by a particle in a Millikan condenser, as the device may be called, is easily detectable. Hence a Millikan condenser is the most sensitive apparatus known for the measurement of minute quantities of electricity. Kelly[1] and Lukirsky and his collaborators[2] are among those who have used the Millikan condenser successfully for the determination of the photoelectric thresholds of non-conductors. The method is limited by the fact that the material must be obtainable in a finely divided form and by the fact that air, or some other gas, at a pressure of the order of one atmosphere, is essential. Consequently, it is inherently impossible to apply the method to the study of outgassed substances in a vacuum.

Certain chemical compounds have been studied in a variety of forms. Thus a substance may be investigated as a chemically pure crystal, or as a powder, or as a capsule produced by compressing the powder under extremely high pressures, or as a mineral either with its "natural" surface or with a freshly exposed surface. The photoelectric currents vary greatly, showing once again that the state of the surface is an all-important factor. A much larger photoelectric current is obtainable from powder highly compressed into a capsule or solid block than from the loose powder.

10-2. Elements and Simple Inorganic Compounds.—The surface photoelectric effect has been investigated for but few non-metallic elements, and the results have been qualitative rather than quantitative. Goldmann and Kalandyk[3] using an apparatus similar to that shown in Fig. 10-1 obtained a photoelectric effect for sulphur when illuminated by ultra-violet light, but not when illuminated by light passing through glass (limit about 3300A). This is in accord with the results of Kelly,[4] who used a Millikan condenser and found the threshold to be between 2200A and 2400A. Hughes[5] found the thresholds of arsenic and selenium, both distilled in vacuum, to be 2360A and 2200A, respectively. The threshold for carbon in the form of soot is 2550A (Hughes).

Oxides vary widely in their photoelectric characteristics. Oxides of light metallic elements and of the alkali and alkaline-earth metals appear to be photoelectrically insensitive to the accessible ultra-violet ($\lambda > 2000$A). On the other hand, photoelectric currents of the same order as those obtained from metals are recorded for oxides of certain heavy metals. It is suggested that perhaps the more stable an oxide is, as measured by its heat of formation, the farther in the ultra-violet is its

[1] M. J. Kelly, *Phys. Rev.*, **16**, 260 (1920).

[2] P. Lukirsky, N. Gudris, and L. Kulikowa, *Zeits. f. Phys.*, **37**, 308 (1926); N. Gudris and L. Kulikowa, *Zeits. f. Phys.*, **45**, 801 (1927).

[3] A. Goldmann and S. Kalandyk, *Ann. d. Phys.*, **36**, 589 (1911).

[4] M. J. Kelly, *Phys. Rev.*, **16**, 260 (1920).

[5] A. L. Hughes, *Phil. Mag.*, **24**, 380 (1912).

threshold. Hallwachs[1] found that the photoelectric currents from CuO and Cu_2O were of the same order as those from Cu. Similarly, PbO_2 has a photoelectric effect comparable to that of metals (Wilson,[2] Hallwachs[1]). (In both cases the material was in air and was illuminated by the light from a carbon arc.) Millikan[3] found the threshold for oxidized copper to be between 2530A and 2690A. From the spectral distribution curves obtained by Fleischmann[4] for CuO and Cu_2O, we estimate the thresholds to be 2310A and 2400A, respectively. Hughes[5] found that dry P_2O_5, sublimed in vacuum, was not photoelectrically active when illuminated by light from a mercury lamp (shortest wave-length about 1850A), but became quite active after exposure to moist air. Results for a number of oxides obtained under comparable conditions will be found in Table 10-2.

The sulphides have been investigated qualitatively by Rohde.[6] When illuminated by light from a zinc spark, the relative photoelectric currents listed in Table 10-1 were obtained.

TABLE 10-1.—RELATIVE PHOTOELECTRIC CURRENTS FROM SULPHIDES[1,2]

PbS	887	FeS_2	176	CoAsS	89		
Cu_2S	534	Cu_2S_3	160	ZnS	80		
CuS	391	MnS_2	141	FeS	64	Zn^3	530
MnS	355	Bi_2S_3	138	CdS	58		
Ag_2S	240	Fe_7S_8	122	Sb_2S_5	45	Al^3	200
SnS	236	NiS	102	CoS	29		
				MoS	28		

[1] All observations made in air.
[2] Sulphides either mineral or chemically prepared, and then highly compressed.
[3] Results for metallic Zn and Al recorded for comparison.

Results qualitatively in accord with the foregoing have been obtained by Knoblauch, Ramsey and Spencer, Wilson, and Herrmann.[7] The last found that the tellurides and selenides gave photoelectric currents comparable with the sulphides. As examples of sulphides which give *no* photoelectric currents when they are illuminated by light from a zinc spark in air (shortest wave-length probably 1700A), we have the sulphides of all the alkaline-earth metals (Schmidt).[8] It may be inferred from curves given in a paper by Fleischmann[4] that the threshold of Ag_2S is at 2600A.

[1] W. HALLWACHS, *Ann. d. Phys.*, **37**, 666 (1889); *Phys. Zeits.*, **5**, 493 (1904).
[2] W. WILSON, *Ann. d. Phys.*, **23**, 107 (1907).
[3] R. A. MILLIKAN, *Phys. Rev.*, **7**, 366 (1916).
[4] R. FLEISCHMANN, *Ann. d. Phys.*, **5**, 73 (1930).
[5] A. L. HUGHES, *Phil. Mag.*, **24**, 380 (1912).
[6] O. ROHDE, *Ann. d. Phys.*, **19**, 952 (1906).
[7] O. KNOBLAUCH, *Zeits. f. Phys. Chem.*, **29**, 527 (1899); W. RAMSEY and J. F. SPENCER, *Phil. Mag.*, **12**, 397 (1906); W. WILSON, *Ann. d. Phys.*, **23**, 124 (1907); K. HERRMANN, *Dissertation*, Berlin (1908).
[8] G. C. SCHMIDT, *Ann. d. Phys.*, **64**, 708 (1898).

A number of investigations on various common inorganic compounds are on record. As a general rule the conditions under which the investigations were carried out are far from comparable, which makes it difficult to draw satisfactory conclusions. The results of Dima[1] are of value in that he measured the photoelectric currents from numerous compounds under identical conditions. These compounds were all in the form of capsules of compressed powder. Because in many cases the photoelectric current changes progressively with the duration of the illumination, it was considered best always to give the *initial* values of the currents as being more strictly comparable (Table 10-2).

TABLE 10-2.—RELATIVE PHOTOELECTRIC CURRENTS FROM COMPOUNDS[1]

HgI_2	10	HgI	112	CuO	4,800	Cu_2O	14,400
$HgCl_2$	2	$HgCl$	12	$CuCl_2$	10	$CuCl$	50,000
HgO	7	Hg_2O	280				
$Hg(C_6H_5CO_2)_2$	12	$Hg(C_6H_5CO_2)$	18	PbO_2	1,700	PbO	3,200
SnO_2	24	SnO	1,220	CrO_3	1	Cr_2O_3	50
SnS_2	186	SnS	1,440				
				BiO_3	70	Bi_2O_3	110
Fe_2O_3	202	FeO	7,200				
$FeCl_3$	1	$FeCl_2$	26	MnO_2	48	Mn_3O_4	130
						MnO	500

[1] Illumination from a quartz mercury lamp.

The principal conclusion to be drawn from these results is that when a metal can combine with another element in two ways, the compound in which the metal has the lower valence has the bigger photoelectric effect. In the absence of direct experimental evidence we may tentatively associate the bigger photoelectric effect with a threshold of a longer wave-length. If this be a correct procedure, then the electrons are more easily separated from the compounds in which the metal has a lower valence, a view which is in harmony with the usual chemical picture of the connection between electrons and valence. Dima measured the photoelectric currents from the halides of a number of metals, and concluded that in almost all cases the iodides gave the largest currents, the bromides came next, and the chlorides gave the least. The same result was obtained by Pochettino for the halides of copper.[2]

An investigation of the photoelectric effects of salts distilled in vacuum was made by Hughes.[3] The unresolved light from a quartz mercury lamp was used. In the case of HgI_2, HgI, $HgCl_2$, $HgCl$, and BiO_3, it was found that the photoelectric current was initially zero or quite small and that it increased steadily with the time.[4] After prolonged

[1] G. A. DIMA, *Comptes Rend.*, **176**, 1366 (1913); **177**, 598 (1913).

[2] A. POCHETTINO, *Accad. Lincei, Atti*, **15**, 355 (1906).

[3] A. L. HUGHES, *Phil. Mag.*, **24**, 380 (1912).

[4] Reboul also found that the photoelectric effects for the halides of copper and silver increased with the time of exposure to light (*Le Radium*, **10**, 155 [1912]).

exposure to light the surfaces had in many cases a gray metallic luster, indicating that photochemical decomposition of the compound had been produced. Evidently the growing photoelectric effect observed should be attributed to the metal set free photochemically. The salts themselves are probably inactive. PbI_3 showed a small effect of the same kind and $FeCl_3$ a barely perceptible one. Distilled $ZnCl_2$ and P_2O_5 showed no photoelectric effect and no photochemical decomposition. The only distilled compound which gave a large initial photoelectric current was SbI_3 and, contrary to the behavior of the other distilled salts, its photoelectric effect diminished with the time of exposure.

The photographic activity of the silver halides has led to several investigations of their photoelectric properties. Large photoelectric effects have been observed in AgCl, AgBr, and AgI, by Schmidt[1] (using light from a spark) and by Toy and his collaborators[2] (who used a quartz mercury lamp). The former found much the same photoelectric current for each, the latter, however, found currents in the ratio of 1:10:100, sandpapered silver giving a value of 200 under the same conditions. Toy found the threshold for each substance to be below 2800A. (The other limit is probably about 2000A, since a quartz mercury lamp was used.) The curves given by Fleischmann[3] indicate that the thresholds for AgI, AgBr, and AgCl are approximately at 2500A, 2350A, and 2310A, respectively. Wilson[4] investigated the surface photoelectric effect for AgI simultaneously with the photoconductivity. The latter was produced both by ultra-violet light and by visible light, but mainly by visible light. The surface photoelectric effect, however, required ultraviolet light to bring it out. Clearly more energy is required to release an electron inside AgI and to bring it through the surface than merely to set it free inside; in other words, the surface of the salt has a work function just like a metal.

Most compounds of the alkali metals and the alkaline-earth metals, as well as nitrates, sulphates, and carbonates of the heavy metals, are generally said to be inactive photoelectrically. However, more sensitive methods of measuring small currents and the use of sources of light rich in short wave-lengths will no doubt transfer many of these salts to the list of photoelectrically active substances. Using the very short wave-lengths transmitted by fluorite (1500A?) from a mercury lamp, Zimmermann[5] found the ferrocyanides to be unusually active photoelectrically, while certain other salts, usually considered to be inactive, gave measurable currents. The currents obtained from $K_4Fe(Cn)_6 \cdot 3H_2O$, Na_4-

[1] G. C. Schmidt, *Ann. d. Phys.*, **64**, 708 (1898).
[2] F. C. Toy, H. A. Edgerton, and J. O. C. Vick, *Phil. Mag.*, **3**, 482 (1927).
[3] R. Fleischmann, *Ann. d. Phys.*, **5**, 73 (1930).
[4] W. Wilson, *Ann. d. Phys.*, **23**, 107 (1907).
[5] W. Zimmermann, *Ann. d. Phys.*, **83**, 329 (1926).

$Fe(CN)_6 \cdot 10H_2O$, KI, KBr, $FeSO_4$, $Na_2Cr_2O_7$, $NaClO_3$, and $CuSO_4$ were in the ratios 1000: 450: 410:240: 40: 30: 18: 10.

Predwoditelew and Blinow[1] found that water of crystallization was a significant factor in determining the photoelectric current from certain salts. $CuSO_4 \cdot 5H_2O$, $AlK(SO_4)_2 \cdot 12H_2O$, and $Pb(C_2O_2H_3)_2 \cdot 3H_2O$ lose their water of crystallization slowly in a vacuum. The loss of water was determined by a microbalance, and it was found that the photoelectric current increased as the water disappeared, but only up to a certain point, for, on starting with an anhydrous salt, the photoelectric current increased as it took up water of crystallization until about one molecule of water had been taken up by each molecule of the salt. Spectral distribution curves were not determined, nor was any attempt made to determine thresholds.

These authors attempted to interpret their results in terms of the absorption of the water molecules surrounding each salt molecule. By applying the Thomson-Whiddington law of absorption of electrons they were able to account for their results quantitatively. It seems, however, that this is a doubtful procedure, for this law governs the change in *velocity* of relatively fast electrons and what they measure is the total *number* of electrons emerging.

Werner[2] and Erbel[3] have applied the methods of modern high-vacuum technique to the study of the photoelectric currents from CdI_2, $PbCl_2$, and KNO_3, when illuminated by light from a quartz mercury lamp. The photoelectric currents diminished rapidly with the exposure, owing to the loss of electrons by the surfaces which left them positively charged. When this had been allowed for, it was found that, just as in the case of many metals, outgassing a salt, first, increased the photoelectric current, and then diminished it ultimately to zero. It is unfortunate that no attempt was made to study the corresponding threshold shifts. Admission of dry gases did not restore the photoelectric current; to bring it back it was necessary to expose the salts to water vapor. This result is in accord with that recorded by Hughes[4] who found that P_2O_5 and $ZnCl_2$ sublimed in vacuum gave no photoelectric current when illuminated by light from a mercury lamp, but that exposure to water vapor made both substances photoelectrically active. These results, together with those of Predwoditelew and Blinow[5] on the exposure of anhydrous salts to water vapor, show that in some way the H_2O molecule (although the threshold for pure water is about 1700A or less) diminishes the work function of a number of substances.

[1] A. Predwoditelew and W. Blinow, *Zeits. f. Phys.*, **42**, 60 (1927); **44**, 207 (1927).

[2] J. Werner, *Zeits. f. Phys.*, **57**, 192 (1929).

[3] H. Erbel, *Zeits. f. Phys.*, **66**, 59 (1930).

[4] A. L. Hughes, *Phil. Mag.*, **24**, 380 (1912).

[5] A. Predwoditelew and B. Blinow, *Zeits f. Phys.*, **42**, 60 (1927); **44**, 207 (1927).

The thresholds of a number of crystals have been determined by Lukirsky, Gudris, and Kulikowa[1] by means of a Millikan condenser.

TABLE 10-3.—THRESHOLDS FOR SALTS

Salt	Threshold	E, cal/mol	Thresholds	
			Before illumination	After illumination
I	II	III	IV	V
LiF	1860A	254		
NaF	1940A	220		
RbI	1940A	196		
NaCl	2013A	181	2098A	2210A
KCl	2013A	165	2098A	2210A
RbCl	2044A	160		
CsCl	2044A	154		
CuCl	1895A	232		
NaBr	2031A	169	2116A	2210A
KBr	2044A	154	2044A	2098A
CuBr	1988A	223		
$CdBr_2$	1860A	617		
NaI	2040A	156	2116A	2116A
KI	2116A	143	2098A	2116A
RbI	2210A	139	2210A	2275A
CsI	2210A	134	2210A	2275A

Column II. Mean thresholds from upper and lower limits given in the paper by Lukirsky, Gudris, and Kulikowa (1926).

Column III. Energy of the lattice.

Column IV. Mean thresholds from upper and lower limits given in the paper by Gudris and Kulikowa (1927) *before* illumination.

Column V. *Idem*, but *after* prolonged intense illumination by ultra-violet light.

Into this they introduced a small amount of a freshly powdered crystal. The loss of a photoelectron by a particle held suspended was revealed in the usual manner as a discontinuous change in its state of motion. Spectrally resolved light did not give enough energy to allow determination of the thresholds; they were therefore determined by means of light filters whose short wave-length limits were known.

A comparison of the figures given in Columns II and III (Table 10-3) shows a certain parallelism between the work necessary to detach a photoelectron from these salts and the energy of the lattice.

[1] P. LUKIRSKY, N. GUDRIS, and L. KULIKOWA, *Zeits. f. Phys.*, **37**, 308 (1926); N. GUDRIS and L. KULIKOWA, *Zeits. f. Phys.*, **45**, 801 (1927).

Gudden[1] calls attention to the fact that it is peculiar that rocksalt, according to these experiments, has a photoelectric effect in a region in which Hilsch found no measurable absorption. (It is true that Hilsch examined large clear crystals, whereas the photoelectric experiments were made on pulverized crystals. The act of pulverization may have introduced some contamination; if not, we may have to consider that photoelectric characteristics may be altered by pulverizing a crystal.)

Prolonged illumination causes the threshold to shift by a small but definite amount towards longer wave-lengths, as shown in Columns IV and V. Exposure to strong visible light, on the other hand, shifts the threshold back again. The shift in the spectral distribution curve for photoconductivity towards the red, when a crystal is illuminated by light capable of inducing a volume photoelectric effect, and its return when the crystal is flooded by red or infra-red light, is a familiar phenomenon in photoconductivity (Chapter VIII). It is probable, therefore, that in a crystal the surface photoelectric effect and the volume photoelectric effect are closely related, and that, in all probability, the photoelectron which comes through the surface is one which has been set free within the crystal and which, with a suitable field, would have taken part in the photoconductivity. The thresholds for rocksalt treated in various ways are given in Table 10-4.

TABLE 10-4.—THRESHOLDS OF COLORED ROCKSALT

Rocksalt	Threshold
Chemically prepared, unilluminated	2098A
Illuminated by ultra-violet light	2142A
Slightly colored by X-rays	2142A
Slightly colored by γ-rays	2142A
Strongly colored by X-rays	5000A to 4000A
The latter, bleached by daylight	2098A
Blue rocksalt (mineral)	2275A
Electrolytically colored	2275A

The position of the threshold for rocksalt, which has been strongly colored by exposure to X-rays, is not far from that at which the photoconductivity is a maximum. This implies that the work necessary to take a photoelectron through the surface of this particular kind of rocksalt is abnormally small. This unexpected result suggests the desirability of further investigation.

Some interesting experiments, bearing on the work functions of crystals, have been made by Tartakowsky.[2] He found that rocksalt crystals were inactive photoelectrically when illuminated by a mercury lamp. Assuming the shortest wave-length available to be about 2000A, this would lead to a work function of over 6 volts. If now the rocksalt

[1] B. GUDDEN, "Lichtelektrische Erscheinungen," p. 115 (Julius Springer, 1928).
[2] P. TARTAKOWSKY, *Zeits. f. Phys.*, **58**, 398 (1929).

crystal be bombarded by electrons from a hot wire in the same vacuum, the crystal shows a considerable photoelectric current which diminishes slowly with the time. The photoelectric effect—if we may call it so—ceases when the surface has been completely discharged. It has a clearly marked threshold (>3020A, <3130A) corresponding to a work function of 4.2 volts. This seems to be independent both of the density of the electron stream and of the energy of the electrons (5 to 100 volts). Tartakowsky suggests that the work function of a crystal may be divided into two parts: W_1, the work necessary to set an electron free within a crystal and bring it to the surface; and W_2, that necessary to take it from the surface. On his view, W_2 is measured when he determines the threshold of a rocksalt surface charged with electrons. Since $W_2 = 4.2$ volts and $W_1 + W_2 > 6$ volts, it is evident that $W_1 > 1.8$ volts. The latter would correspond to a wave-length shorter than 6800A. Since clear rocksalt does not have a measurable absorption, and therefore, in accord with experiment, no photoconductivity in the visible,[1] the value of W_1 cannot be checked directly. Indirect support as to the order of W_2 is perhaps given by the fact that visible light (3000A to 5000A) produces a strong photoconductivity in *colored* rocksalt.[2]

Certain puzzling difficulties are raised when we come to inquire into the nature of the work function of an insulator. The explanation in terms of the forces between an electron and its image, so satisfactory in the case of metals, becomes somewhat strained when we recall that an image requires a conductor. In the case of Tartakowsky's experiments the photoelectrons do not even come through the surface; they are on the surface to begin with. It is possible that the electrons driven on to the surface accumulate on those positions which are just over the positive ions of the surface lattice, and are held there by forces which correspond to the measured work function.

10-3. Other Solids.—We shall record briefly in this section a few miscellaneous results relating to the photoelectric properties of a number of solids, which, for the most part, cannot be classified as simple compounds. Shellac has been found to be photoelectrically active when illuminated by ultra-violet light (Wilson,[3] Goldmann and Kalandyk,[4] Kelly[5]). Kelly, who used a Millikan condenser, found its threshold to be on the short wave-length side of 2200A. Reiger[6] recorded photoelectric effects for ebonite, mica, sealing wax, and resin when illuminated by a carbon arc. Kelly found paraffin and paraffin oil to have a threshold

[1] Sec. **8-11**.
[2] Sec. **8-13**.
[3] W. Wilson, *Ann. d. Phys.*, **23**, 107 (1907).
[4] A. Goldmann and S. Kalandyk, *Ann. d. Phys.*, **36**, 589 (1911).
[5] M. J. Kelly, *Phys. Rev.*, **16**, 260 (1920).
[6] R. Reiger, *Ann. d. Phys.*, **17**, 935 (1905).

between 2150A and possibly 1750A. Hughes[1] found the threshold of anthracene, sublimed in vacuum, to be between 2000A and 2200A.

In recent theories of the photoelectric effect of metals, it is assumed that the photoelectrons are originally the free electrons which account for metallic conduction. It is conceivable, therefore, that there might be a characteristic difference between the photoelectric effects of solids which are metallic or *electronic* conductors, and of those which are electrolytic or *ionic* conductors. With this in mind, Fleischmann[2] investigated the photoelectric effects for CuO, Cu_2O, and Cu which are electronic conductors, and for AgI, AgBr, and AgCl which are ionic conductors. He also investigated Ag_2S at various temperatures, for above 179°C its conductivity is entirely ionic; below 179°C it is 20 per cent electronic. He found that the photoelectric yield did not change appreciably as he passed through this transition point. He also verified Einstein's equation for photoelectrons from ionic conductors, as well as for those from electronic conductors. No characteristic difference in the shapes of the spectral distribution curves for the two types of conductor could be observed. The conclusion therefore is that, though two substances may conduct in a fundamentally different manner, there is no outstanding difference in the kind of photoelectric effect they show.

Fleischmann's spectral distribution curves indicate that the thresholds for solid cyanine and fuchsine are 2350A and 2980A, respectively.

Certain chemically non-homogeneous substances possess marked photoelectric properties. As examples of such substances may be cited colored rocksalt, in which there are colloidal particles of sodium here and there in the crystal lattice, and the highly phosphorescent "Lenard phosphors." A representative phosphor (CaBiS) is pure calcium sulphide to which a flux and a trace of bismuth have been added, and the whole fused together. Balmain's luminous paint contains such a phosphor. Elster and Geitel in 1892 observed that Balmain's paint and many phosphorescent minerals had marked photoelectric activity. A systematic investigation of phosphors was made by Lenard and Saeland.[3] They obtained satisfactory evidence for the view that the light which produces a photoelectric effect is also that which produces a phosphorescence.[4] Absorption of light by a "center" containing a speck of metal leads to the ejection of an electron which becomes embedded in the surrounding insulator. The return of the electron, later, is accompanied by the emission of phosphorescent light. When these centers are on the surface the electrons may escape altogether; thus we have a

[1] A. L. Hughes, *Phil. Mag.*, **24**, 380 (1912).

[2] R. Fleischmann, *Ann. d. Phys.*, **5**, 73 (1930).

[3] P. Lenard and S. Saeland, *Ann. d. Phys.*, **28**, 476 (1909).

[4] The relation between phosphorescence and photoconductivity is discussed in Secs. **8-24** and **8-25**.

photoelectric effect. A more recent investigation has been made by Goeggel.[1] He found that pure CaS was photoelectrically inactive, but that when it was converted into a "CaBiS phosphor" it acquired a remarkable photoelectric sensitivity. Its high insulating power called for a special technique, including the use of a very sensitive electrometer and a very thin layer of material. With continued illumination the photoelectric current diminished. More and more of the centers became excited and fewer and fewer of them were available for absorbing the light. The excitation could be much diminished by the quenching action of infra-red light. (Further discussion on the quenching effect of long wave-length light will be found in the chapter on Photoconductivity.)

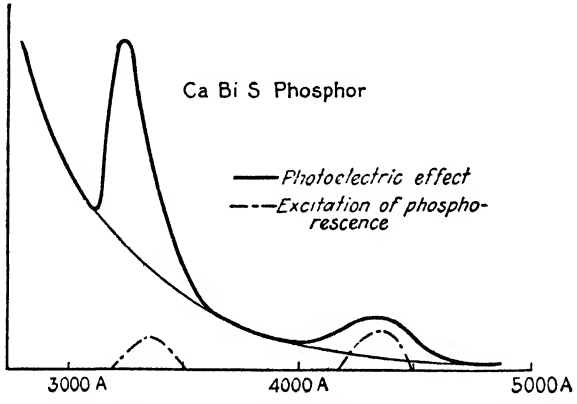


FIG. 10-4.—Photoelectric effect and excitation of phosphorescence.

The spectral distribution curve of the photoelectric effect of a CaBiS phosphor is shown in Fig. 10-4, together with a curve showing the efficiency of various wave-lengths in exciting its α-phosphorescence band (Lenard's d-type excitation). The coincidence of the maxima is strong evidence for the photoelectric basis of Lenard's theory of phosphorescence. By suitable mechanical means, such as rubbing the surface with a file, it is possible to disturb the structure to such an extent that the phosphorescing power is diminished very greatly. When this is done in daylight the phosphor acquires a characteristic color. The photoelectric spectral distribution curve for such a surface now resembles the curve in Fig. 10-4, but *without* the two maxima, *i.e.*, a curve beginning at about 5000A and rising steadily towards shorter wave-lengths. It is significant that this is also the spectral distribution curve for Lenard's u-type excitation. If the filing of the surface is done in the dark, the surface is at first colorless and has a high photoelectric sensitivity, which however diminishes greatly as it becomes colored on exposure to light. Moreover, the spectral distribution of the photoelectric effect is practically coincident

[1] K. GOEGGEL, *Ann. d. Phys.*, **67**, 301 (1922).

with that of the efficiency of light of different wave-lengths in producing the characteristic color of this "*druckzerstörter*" phosphor.

10-4. Inorganic Liquids.—Water does not begin to absorb light strongly until we get to 1750A. Consequently we should not expect to find a photoelectric effect in water with the usual sources of ultra-violet light. This is in agreement with some early experimental results (Brillouin,[1] Hughes[2]). According to Obolensky,[3] a small photoelectric effect is obtained when light from a spark, filtered through a fluorite window and about 5 mm of air, is used (shortest wave-length possibly between 1250A and 1500A). This, however, may be spurious, for, according to the recent work of Zimmermann,[4] light of wave-length 1650A does not produce a photoelectric effect in freshly distilled water. A photoelectric effect appears on standing and grows; its characteristics suggest that it is to be attributed to the accumulation of invisible solid particles on the surface.

Both Brillouin and Obolensky find a strong photoelectric effect in ice. According to the latter, the photoelectric current from ice is about 300 times greater than that from water when both are illuminated by light transmitted through fluorite from a spark. From the filters used by Obolensky in these experiments, we estimate the threshold for ice to be between 1800A and 2000A.

Obolensky found that the weak effect in pure water was diminished further by the addition of NaCl and KCl, but increased from two- to four-fold by the addition of sulphates, carbonates, and nitrates of the same bases. These results, however, are not in accord with those of Zimmermann.[4] Over twenty salts dissolved in water were tested, and it was found that, except with the ferrocyanides, no photoelectric effect could be detected when the surface was fresh (shortest wave-length 1650A). Consistent photoelectric effects were obtained with solutions of the ferrocyanides of lithium, sodium, and potassium. Strong fatigue was noticed with ordinary solutions of these salts, but not after the solutions had been filtered through a membrane filter of the Szigmondy type to remove colloidal particles. (In the latter case the current remained constant for many hours.) The slow accumulation of solid particles on the surface was avoided in some experiments by forcing the solution through a funnel from the bottom, so that there was a constant overflow at the top, thus exposing a new surface continuously. The photoelectric current increased somewhat more rapidly than the concentration of the ferrocyanide in solution. This suggested that the *undissociated* molecules were chiefly responsible for the photoelectric effect, a view which received support when it was found that the addition of KI, itself inactive photo-

[1] M. Brillouin, *Meteor. Zeits.*, **25**, 38 (1908).
[2] A. L. Hughes, *Phil. Mag.*, **24**, 380 (1912).
[3] W. Obolensky, *Ann. d. Phys.*, **39**, 961 (1912).
[4] W. Zimmermann, *Ann. d. Phys.*, **80**, 329 (1926).

electrically, to the ferrocyanide solution, increased the effect since it is known that this tends to suppress the dissociation of the ferrocyanide.

10-5. Organic Liquids.—Organic dyes and some of their solutions were found to be photoelectrically active very soon after the photoelectric effect was discovered (Hallwachs[1]). Aqueous solutions of methyl violet, cyanine, and fuchsine showed large effects. The nature of the solvent is of great importance; for example, when fuchsine is dissolved in water it is photoelectrically active, but not when dissolved in alcohol, although the two solutions fluoresce equally well (Schmidt[2]). It is evident, therefore, that there is no close connection between fluorescence and photoelectric activity in organic dyes. Certain discrepancies were cleared up by the systematic investigations of Rohde.[3] He found that the photoelectric current from a freshly made aqueous solution of fuchsine or methyl violet increased from an initial zero value to a large final value which it approached asymptotically. That this was due to the gradual formation of a thin *solid* film on the surface was shown in the following way: A metal sheet was suspended in the solution by a fine wire hanging from a torsion head. The longer the solution was left standing the stronger was the film, as measured by the amount of torsion necessary to rupture it. The increase with time in the photoelectric activity of the film was so similar to that in its mechanical strength that there was no doubt that the photoelectric effect must be attributed to the solid film. The solution itself was inactive. A solution in alcohol was not photoelectrically active, nor did a solid film form on its surface. Kelly,[4] using a Millikan condenser for his investigation, found paraffin oil had a threshold beyond 2150A. (We may infer from his data that the lower limit was about 1750A.) It is not lack of absorption which is responsible for the absence of a photoelectric effect in hydrocarbons in the accessible ultra-violet, for many of them begin to absorb strongly at about 2500A.

According to Zimmermann,[5] a clear solution of formaldehyde is inactive when first illuminated by short wave-length light (shortest wave-length possibly 1650A). A film of some kind soon forms, however, as a result of photochemical action, and has a photoelectric effect. In an investigation on various materials dissolved or suspended in liquids, Zwaardemaker and Hogewind[6] concluded that a photoelectric effect appeared only (1) when the dissolved material is itself photoelectrically active, (2) when the solution absorbs the light strongly, and (3) when

[1] W. Hallwachs, *Ann. d. Phys.*, **37**, 666 (1889); *Phys. Zeits.*, **5**, 493 (1904).
[2] G. C. Schmidt, *Ann. d. Phys.*, **64**, 708 (1898).
[3] O. Rohde, *Ann. d. Phys.*, **19**, 935 (1906).
[4] M. J. Kelly, *Phys. Rev.*, **16**, 260 (1920).
[5] W. Zimmermann, *Ann. d. Phys.*, **80**, 329 (1926).
[6] H. Zwaardemaker and F. Hogewind, *Proc. Amst. Acad. Sci.*, **21**, 1146 (1919).

the solution is a colloidal solution. Typical materials used in forming colloidal solutions were blood, albumen, and gelatin.

The net result of the investigations discussed in this and the preceding sections is that no liquid, whether organic or inorganic, has been found to show a genuine photoelectric effect (with light of wave-length longer than about 1700A), except in the single case of solutions of the ferrocyanide salts. When a photoelectric effect has apparently been obtained it has been found due to a solid film or colloidal particles on the surface.

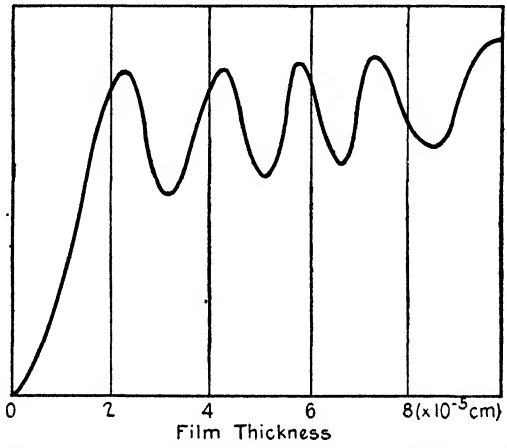


FIG. 10-5.—Photoelectric current from fuchsine as a function of film thickness.

10-6. Aniline Dyes.—Remarkable fluctuations in the photoelectric currents from thin films of dyestuffs as a function of the thickness of the layer were found by Predwoditelew and Netchaewa.[1] Known amounts of solutions of dyes (*e.g.*, fuchsine, crystal violet, etc.) in alcohol were allowed to evaporate on a silver disk, leaving behind a thin film whose thickness could easily be calculated. The photoelectric currents were produced by illumination with the unresolved light of a quartz mercury lamp. Typical results are shown in Fig. 10-5. Explanations on the basis of the production of standing waves in the thin films were offered by Hlucka[2] and by Akulov.[3] The argument may be briefly summarized as follows: If we consider a thin film, bounded by two homogeneous media, classical optical theory gives a definite value to the time average of the light energy at each place in the film. This value, which is expressed as a complicated function of the optical constants of all three media concerned, is a periodic function of the thickness of the film as well as of the distance from the incident face. Knowing the optical constants for 3650A and 4040A (to which he arbitrarily attributed the photoelectric

[1] A. PREDWODITELEW and N. NETCHAEWA, *Zeits. f. Phys.*, **29**, 332 (1924).
[2] F. HLUCKA, *Zeits. f. Phys.*, **38**, 589 (1926).
[3] N. AKULOV, *Zeits. f. Phys.*, **41**, 920 (1927).

effect), and making plausible assumptions as to the absorption coefficient of the electrons, Akulov obtained the curve C (Fig. 10-6), which is the sum of A and B for the monochromatic rays considered. In spite of the agreement between theory and experiment, we must regard it as largely accidental, since the photoelectric threshold of the dyes is almost certainly far in the ultra-violet, and the optical constants of the active

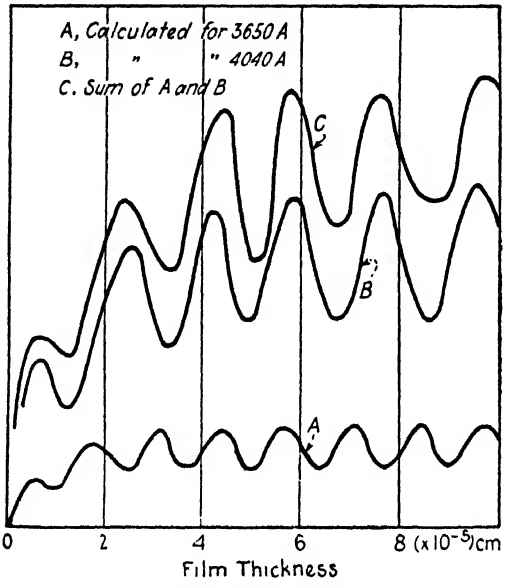


FIG. 10-6.—Photoelectric current (fuchsine).

rays are probably quite different from those assumed. Nevertheless, the investigation is valuable in that it undoubtedly shows that in a complete theory of the photoelectric effect in thin films standing waves may play an important part. It is quite possible that the maxima in the photoelectric currents from thin films of platinum on glass, as studied by Stuhlmann and others, may be interpreted in terms of standing waves if one knew the optical constants to use (Sec. **14-1**).

CHAPTER XI

PHOTOELECTRIC EFFECTS OF X-RAYS AND γ-RAYS

While in this book we are concerned primarily with the photoelectric effects of visible and ultra-violet light, no discussion of the subject of photoelectricity would be complete without a brief reference to the effects observed with radiation of higher frequencies. Some idea of the extent and fundamental importance of this field may be suggested by listing a few of its major accomplishments:

1. The Einstein equation has been precisely confirmed for photoelectrons ejected by all frequencies up to those of the hardest γ-rays—thus establishing it as one of the most far-reaching and fundamental relations in all physics.

2. It has been discovered that the Einstein equation holds also for the inverse photoelectric process (the production of radiation, *e.g.*, X-rays, by electrons), and this discovery has yielded a highly precise method for determining the value of Planck's constant.

3. By measuring the velocity of photoelectrons ejected from atoms by X-rays and γ-rays it has been found possible to obtain directly accurate experimental values for the atomic energy levels, and also for the wavelength of the incident radiation. In some cases these cannot be accurately determined by any other method.

4. Experiments have yielded information as to the nature of the photoelectric process itself which could never have been obtained through experiments with ultra-violet light.

The reader must obviously be referred to other sources[1] for an adequate review of this field. We shall briefly discuss in this chapter a few of its more important aspects, particularly those which have served to throw light on the fundamental nature of the photoelectric effect itself.

11-1. Experimental Methods.—Although the differences between the photoelectric effects due to light and those due to X-rays and γ-rays are essentially differences in degree rather than in kind, yet the differences in degree are often so great as to require an entirely different type of

[1] A thorough review of this subject has recently been published by F. Kirchner, *Handbuch der Experimentalphysik*, Vol. XXIV (Leipzig Akademische Verlagsgesellschaft, 1930); see also A. H. Compton, "X-rays and Electrons," Chap. VIII (D. Van Nostrand Company, Inc., 1925); and A. Becker, *Handbuch der Experimentalphysik*, Vol. XXIII (Leipzig Akademische Verlagsgesellschaft, 1928).

experimental procedure for their study. In the first place, there will be obvious differences in the methods of producing, transmitting, and monochromatizing the incident radiation. In the second place, the methods of collecting and analyzing the ejected electrons will also differ widely; for, while photoelectrons are ejected by visible light with energies usually less than 1 volt, γ-rays are capable of ejecting electrons with energies of several million volts. It will be of interest to point out the experimental methods which have been most widely used for analyzing the direction and magnitude of the velocities of high-speed photoelectrons.

In some of the early work[1] in this field the photoelectron velocities were measured by the stopping-potential methods similar to those used in experiments with optical frequencies. Because of the high voltages

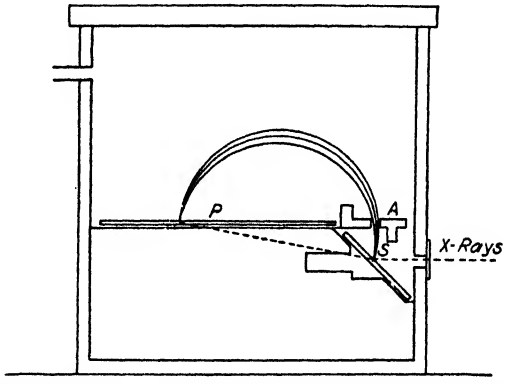


FIG. 11-1.—Magnetic spectrograph for analyzing X-ray photoelectrons. (*de Broglie.*)

required, however, this method is limited for practical reasons to experiments with relatively soft X-rays, and it has not been used in the more recent work. (The electrostatic deflection method recently developed by Hughes, Rojansky, and McMillen[2] should, however, be of use in this field.) The magnetic deflection method originally developed by Classen[3] for measurement of the ratio e/m for cathode rays was first applied to the analysis of photoelectron velocities by Robinson and Rawlinson,[4] and later by de Broglie[5] and others[6] with marked success. A typical experimental arrangement is shown in Fig. 11-1. Electrons are ejected by the incident X-rays from a thin metal ribbon at S. Those coming off within a certain range of angles pass through the slit at A and describe

[1] J. LAMB, *Ann. d. Phys.*, **26**, 712 (1908); W. SEITZ, *Phys. Zeits.*, **11**, 705 (1910).

[2] A. L. HUGHES, V. ROJANSKY, and J. H. MCMILLEN, *Phys. Rev.*, **34**, 284 and 291 (1929).

[3] J. CLASSEN, *Phys. Zeits.*, **9**, 762 (1908).

[4] H. ROBINSON and W. F. RAWLINSON, *Phil. Mag.*, **28**, 277 (1914).

[5] M. DE BROGLIE, *Jour. d. Phys. et Rad.*, **2**, 265 (1921).

[6] R. LEDRUS, *Comptes Rend.*, **176**, 383 (1923); R. WHIDDINGTON, *Phil. Mag.*, **43**, 1116 (1922); H. ROBINSON, *Proc. Roy. Soc.*, **104**, 455 (1923).

circular orbits under the influence of a magnetic field perpendicular to the plane of the diagram. The feature of this method lies in the fact that, after traversing a semicircle under the influence of the field, all electrons of a particular velocity are refocused on the photographic plate P along a line parallel to the source S. In this way a "velocity spectrum" of the photoelectrons is recorded on the plate. The radius of the path traversed by electrons which are refocused at any given point on the plate is determined by direct measurement, and from this the corresponding velocity is at once computed.

The force on an electron moving with the velocity v in a magnetic field H is simply Hev, and this must equal the centripetal force mv^2/r, where r is the radius of the path and m the mass of the electron. Hence,

$$Hev = \frac{mv^2}{r}$$

or,

$$v = \left(\frac{e}{m}\right)Hr. \tag{11-1}$$

It was pointed out by de Broglie[1] that for high-velocity photoelectrons it is necessary to consider the relativity change of mass with velocity and set

$$m = \frac{m_0}{\sqrt{1-\beta^2}},$$

m_0 being the "rest mass" of the electron and $\beta = v/c$. Equation (11-1) then becomes

$$Hr = \frac{m_0}{e}\frac{\beta c}{\sqrt{1-\beta^2}}.$$

Hence

$$\beta^2 = \frac{(Hre/m_0)^2}{c^2 + (Hre/m_0)^2}. \tag{11-2}$$

For the kinetic energy of the electron we then have,

$$E = m_0c^2\left[\frac{1}{\sqrt{1-\beta^2}} - 1\right] = m_0c^2\left[\sqrt{1 + \left(\frac{Hre}{m_0c}\right)^2} - 1\right] \tag{11-3}$$

In place of the photographic plate, other detecting devices have often been used. Thus Ramsauer,[2] in adapting this method to the analysis of the photoelectrons ejected by ultra-violet light, collected the electrons after deflection in a Faraday cage connected to an electrometer. For registering high-speed electrons Chadwick[3] obtained a greatly increased sensitivity by employing a Geiger counter. Recently Watson and Van den Akker[4] have obtained still greater sensitivity and reliability through the use of the Geiger-Müller tube as a detector, in which as few as 20 electrons per minute could be accurately counted. In addition to the

[1] M. de Broglie, *Jour. d. Phys. et Rad.*, **2**, 265 (1921).
[2] C. Ramsauer, *Ann. d. Phys.*, **45**, 961 (1914).
[3] J. Chadwick, *Verh. d. Deutsch. Phys. Ges.*, **16**, 383 (1914).
[4] J. A. Van den Akker and E. C. Watson, *Phys. Rev.* **37**, 1631 (1931).

increased sensitivity, these counting devices have the advantage that the relative intensities of various portions of the spectrum may be determined directly with considerably greater precision than can be obtained from measurements of the blackening of photographic plates. Since in practice it is not feasible to move the counting device across the spectrum, it is fixed in position and the strength of the magnetic field varied to focus electrons of varying velocities into it. By plotting the "count" as a function of the field a velocity distribution curve is at once obtained.

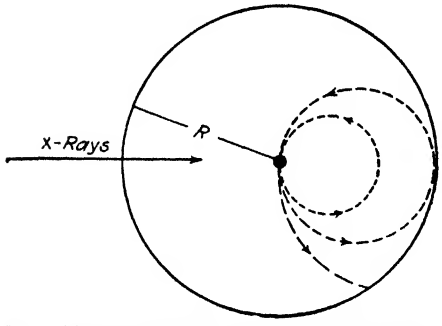


FIG. 11.-2.—Magnetic analyzer for photoelectrons. (*Rudberg.*)

A somewhat different form of magnetic deflection method of analyzing electron velocities has recently been used by Rudberg[1] for his studies in the region of soft X-rays. The electrons are ejected from a wire stretched along the axis of a collecting cylinder (Fig. 11-2), the magnetic field being parallel to the wire. Electrons of varying velocities traverse circular orbits of varying diameters. If the diameter of the orbit is less than the radius of the cylinder the electron will return to the wire, but if greater it will be collected by the cylinder. Thus the current between the wire and the cylinder will consist of only those electrons ejected with a velocity greater than a critical value given by (see Eq. [11-1])

$$v_c = \left(\frac{e}{m}\right)H\left(\frac{R}{2}\right),$$

R being the radius of the cylinder. By varying H and measuring the current to the cylinder a velocity distribution curve is obtained.

For experiments involving a study of the *direction* of ejection of photoelectrons the C. T. R. Wilson[2] cloud expansion chamber has found a wide use. By this well-known method the paths of individual photoelectrons are made visible by the condensation of water vapor on ions produced along the path. A typical photograph showing the ejection of several photoelectrons by a beam of X-rays passing through air is reproduced in Fig. 11-2. If two photographs of the tracks are taken from different angles the direction of the paths in space can be determined. The energy of the individual electrons can be estimated roughly by measuring the length of the path and using the Thomson-Whiddington

[1] E. RUDBERG, *Proc. Roy. Soc.*, **120**, 385 (1928).
[2] C. T. R. WILSON, *Proc. Roy. Soc.*, **87**, 277 (1912).

FIG. 11-3.—Photograph of photoelectron tracks in a Wilson expansion chamber.

relation that the range of the electron is proportional to the square of its kinetic energy.

It will be seen at once that the Wilson chamber offers a beautiful method for studying individual photoelectric processes. While the method is confined to the study of electrons ejected in gases, there is no reason to believe that the *nature* of the photoelectric process itself depends on the type of atom involved or its physical state, *i.e.*, whether it is an atom of argon, or an atom of copper.

11-2. General Results.—It is of interest to analyze the processes which take place when a beam of X-rays (or γ-rays) is absorbed by matter.[1] It is known that the energy in a monochromatic beam is decreased according to the exponential law of absorption,

$$I = I_0 e^{-\mu x},$$

where I_0 is the incident intensity, I the intensity after the beam has traversed a distance x, and μ is the "total absorption coefficient" for the given wave-length. Now energy may be removed from the X-ray beam by two processes, "true absorption" and scattering. In the case of true absorption the energy is actually transformed into other forms, while in scattering it is merely deflected from the beam, but for the most part continues in other directions as X-ray energy. So the total absorption coefficient μ may be broken up into two terms, the true absorption coefficient k, and the scattering coefficient σ. Then,

$$\mu = k + \sigma.$$

The constant μ defined above is known as the *linear absorption coefficient*, since it determines the fraction of the incident beam which will be absorbed per unit length of path. The quotient μ/ρ, where ρ is the density of the absorbing material, is known as the *mass absorption coefficient* (for the given wave-length) and is a constant for a given element or compound regardless of its physical state, *e.g.*, solid, liquid, or gas. The *atomic absorption coefficient*, defined by μ/n, where n is the number of atoms per cubic centimeter, is a constant for a given type of atom regardless of its physical state, *or its state of chemical combination.*[2] It thus appears that the absorption of X-rays is a purely atomic process, and the mechanism of absorption must be sought in the deep-lying electron levels which are unaffected by external conditions.

As a result of many investigations of the absorption coefficients for homogeneous X-rays, it has become well known[3] that the atomic absorp-

[1] *Cf.* A. H. Compton, "X-rays and Electrons," Chap. VI.

[2] Very slight changes of the absorption limits with chemical combination have, however, been detected for the lighter elements.

[3] *Cf.* F. Kirchner, *Handbuch der Experimentalphysik*, Vol. XXIV, pp. 208–230; A. H. Compton, "X-rays and Electrons," p. 187.

tion coefficient varies with the wave-length of the X-rays in the manner shown in Fig. 11-4. As the wave-length of the incident beam increases, the absorption continuously increases, up to a certain critical wave-length where it suddenly decreases to a much lower value. This behavior is

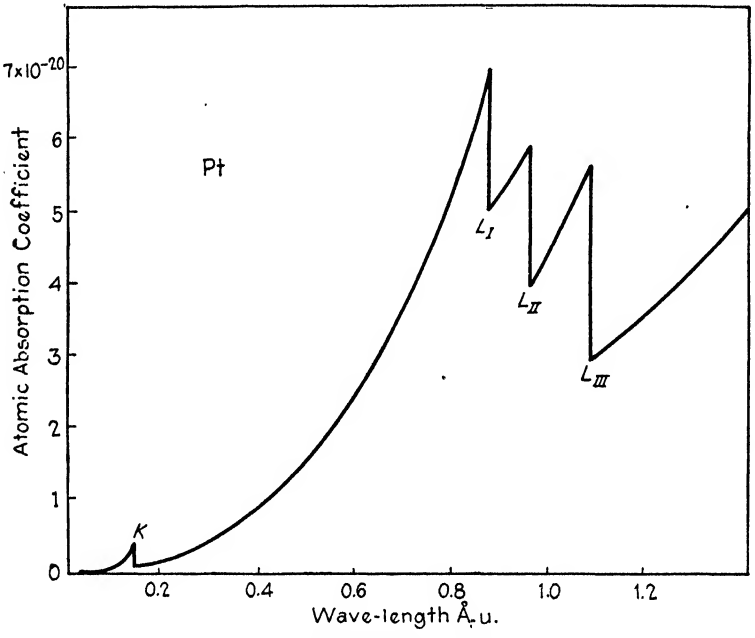


FIG. 11-4.—Absorption of X-rays in platinum. (*From A. H. Compton, "X-Rays and Electrons."*)

repeated through a regular series of critical values. The wave-lengths of these "absorption edges" decrease regularly as the atomic number of the absorber is increased. It turns out in fact that the frequencies of the successive absorption edges are given by relations of the form

$$h\nu_K = W_K,$$
$$h\nu_{L_I} = W_{L_I},$$
$$h\nu_{L_{II}} = W_{L_{II}},$$

etc., where W_K, W_{L_I}, etc. are the energies required to remove an electron from the K, L_I, L_{II}, . . . levels of the atoms of the absorbing material. An X-ray beam then is most strongly absorbed by a given material when the frequency is just great enough to cause the ejection of photoelectrons from some atomic level. This points at once to the obvious conclusion that the absorption of X-rays is due *primarily* to the photoelectric process. This conclusion has been repeatedly verified by experiment, so that it is now a generally accepted fact that the photoelectric process is the *only*

mechanism by which X-rays are truly absorbed. Hence, conversely, every absorbed quantum causes the ejection of a photoelectron.

This statement is not necessarily true for soft X-rays, or for radiation of optical frequencies, for with these, energy can be absorbed by *excitation* as well as *ionization* of atoms. That is, the absorption of low-frequency radiation may simply cause an electron to be lifted from one energy level to another. However, the deeper X-ray levels of all but the lightest atoms are already completely filled, so that a K electron, for example, can be disturbed only by its complete removal.

The statement that every absorbed X-ray quantum causes the ejection of a photoelectron does not mean that all of the *energy* absorbed from the incident beam appears as kinetic energy of the electron, since, of course, much of this energy will be lost in escaping from the atom. As the ionized atom returns to its normal state some of this energy may reappear in the form of "fluorescent" X-rays, characteristic of the absorbing material (see Sec. **11-4**).

The earliest experiments[1] on the energies of photoelectrons ejected by X-rays showed them to be independent of the intensity of the incident beam, but to increase with increased "hardness," *i.e.*, frequency, of the X-rays. This is precisely analogous to the results which had already been obtained for photoelectrons ejected by ultra-violet light. Further experiments[2] have fully confirmed the conclusion that all the fundamental laws of photoelectricity, discussed in Chapter II, are universally valid, regardless of the frequency of the incident radiation. Because of the difficulty of obtaining monochromatic X-ray beams, the exact relation between photoelectron velocity and incident frequency was not quantitatively established until the beautiful work of de Broglie[3] in 1921, who found the maximum energy of emission to be given by the Einstein equation. The earlier work was in complete qualitative agreement with this relation and more recent work has thoroughly confirmed it for frequencies ranging from the softest X-rays[4] to the hard γ-rays.[5] The experimental work will be more fully discussed in the next section. It is of interest to point out, however, that in experiments on the ejection of electrons from metals by *light*, the surface work function p in the Einstein equation,

$$E_{max} = h\nu - p,$$

plays an important rôle, since it is of the same order of magnitude as

[1] P. E. Innes, *Proc. Roy. Soc.*, **79**, 442 (1907); C. A. Sadler, *Phil. Mag.*, **19**, 237 (1910); R. T. Beatty, *Phil. Mag.*, **20**, 320 (1910).

[2] *Cf.* E. Hoepner, *Ann. d. Phys.*, **46**, 577 (1915); F. Kirchner, *Ann. d. Phys.*, **78**, 277 (1925).

[3] M. de Broglie, *Jour. d. Phys. et Rad.*, **2**, 265 (1921).

[4] J. A. Becker, *Phys. Rev.*, **22**, 524 (1923).

[5] C. D. Ellis, *Proc. Roy. Soc.*, **99**, 261 (1921).

$h\nu$. In the case of X-rays, however, $h\nu$ is usually thousands of times larger than p, so that we can write without appreciable error, for the *fastest* electrons ejected from a metal (*i.e.*, those which were initially "free"),

$$E_{max} = h\nu.$$

This means that in X-ray work one is not concerned with surface work functions of metals and their troublesome variations, which, as we have seen, are of such importance in experiments with optical frequencies.

For very soft X-rays, however, such as those excited by cathode rays with a velocity of 500 volts or less, the surface effects are still of importance. A study of the photoelectric effect produced in metals by such X-rays has been made by Richardson and his students,[1] who found marked changes in photoelectric sensitivity due to degassing. Bandopadhyaya has tabulated the photoelectric sensitivities of degassed plates of various metals to 500-volt copper X-rays, listing them in order of decreasing sensitivity as follows: Al, Ag, Fe, Ni, Cu, Au, Pt, Ta, W, Mo, Co, C. The sensitivity of carbon is about one-tenth that of aluminum. Richardson has made extensive use of the photoelectric method in his studies of critical potentials and other phenomena in the soft X-ray region.

11-3. Velocities of Photoelectrons.—The velocity distribution of the photoelectrons ejected by X-rays from solid metal surfaces had been studied previous to 1910 by both the magnetic deflection and the stopping potential method.[2] The observations all showed a continuous distribution curve with most of the electrons emerging with velocities considerably less than that given by the Einstein equation. In fact, the number of faster electrons was found to be so small that the value of the maximum velocity of emission could not be accurately determined. It was found by Seitz[3] and more recently by Simons[4] and Rudberg[5] that, for soft X-rays at least, most of the electrons emerge with velocities less than 3 volts, though the maximum velocity might be as high as several thousand volts. The distribution curve obtained by Rudberg for very soft X-rays ($K\alpha$ line of carbon, for which $h\nu/e = 270$ volts) is shown in Fig. 11-5. It will be noted that there is a very large group of electrons with velocities in the neighborhood of 3 volts and another much smaller group in the neighborhood of the value of 250 volts to be expected from the Einstein equation. Rudberg[5] and Kirchner[6] have

[1] L. P. Davies, *Proc. Roy. Soc.*, **119**, 543 (1928); G. B. Bandopadhyaya, *Proc. Roy. Soc.*, **120**, 46 (1928); O. W. Richardson and F. C. Chalklin, *Proc. Roy. Soc.*, **121**, 218 (1928).

[2] A. Bestelmeyer, *Ann. d. Phys.*, **22**, 437 (1907); P. E. Innes, *Proc. Roy. Soc.*, **79**, 442 (1907); J. Laub, *Ann. d. Phys.*, **26**, 712 (1908); W. Seitz, *Phys. Zeits.*, **11**, 705 (1910).

[3] W. Seitz, *Phys. Zeits.*, **7**, 689, (1906); **11**, 705 (1910).

[4] L. Simons, *Phil. Mag.*, **46**, 473 (1923).

[5] E. Rudberg, *Proc. Roy. Soc.*, **120**, 385 (1928).

[6] F. Kirchner, *Handbuch der Experimentalphysik*, Vol. XXIV, p. 169.

suggested that only the fastest electrons are the true photoelectrons, the slower ones being secondary electrons ejected from the surface by the action of the fastest primaries. Other observers[1] using harder X-rays have not observed the second maximum at the higher velocities but have found only a gradual tailing off of the curve.[2] In spite of the small number of high-speed electrons, however, Kang Fu Hu[3] showed that the curve actually touched the axis within 5 per cent of the value to be

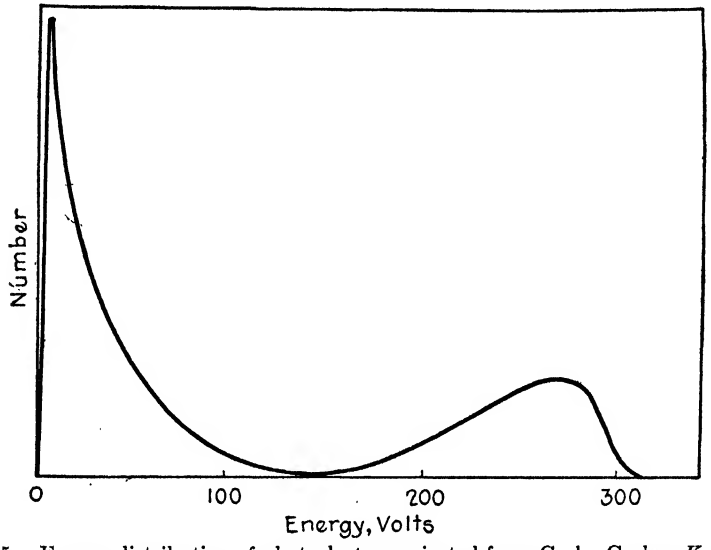


FIG. 11-5.—Energy distribution of photoelectrons ejected from Cu by Carbon $K\alpha$ X-rays. (*Rudberg.*)

expected from the Einstein equation, and there are no experimental results in disagreement with this conclusion.

The most striking tests of the Einstein equation, however, have been made with electrons ejected from thin films of metal. In this case most of the electrons escape from the surface without appreciable energy losses by collision, and what may be called a *primary* velocity distribution is obtained. Using the magnetic deflection method de Broglie[4] first brilliantly showed that the velocity "spectrum" of the electrons ejected from thin films by homogeneous X-rays consists of a continuous background upon which are superposed a number of sharply defined bands or

[1] *E.g.*, W. SEITZ, *loc. cit.*

[2] J. A. BECKER (*Phys. Rev.*, **22**, 524 [1923]) and P. LUKIRSKY (*Zeits. f. Phys.*, **22**, 351 [1924]) have reported a maximum appearing at the high-velocity edge, but there is evidence that, since the X-rays were generated in the same tube in which the photoelectrons were collected, some of the primary cathode rays reached the collecting electrode. These, of course, from the Duane-Hunt relation to be discussed later, would have the velocity of the fastest photoelectrons.

[3] KANG FU HU, *Phys. Rev.*, **11**, 505 (1918).

[4] M. DE BROGLIE, *Jour. d. Phys. et Rad.*, **2**, 265 (1921).

lines. The work of de Broglie has been extended with greatly increased precision in an extensive series of measurements by Robinson and his associates[1] and by Watson and Van den Akker.[2] A particularly good photograph of a magnetic spectrum of electrons ejected from an exceedingly thin (almost invisible) sputtered film of gold is reproduced in Fig. 11-6. It will be noted that many of the lines are quite narrow and are most sharply defined on the high-velocity side. The existence of these lines is explained as follows:

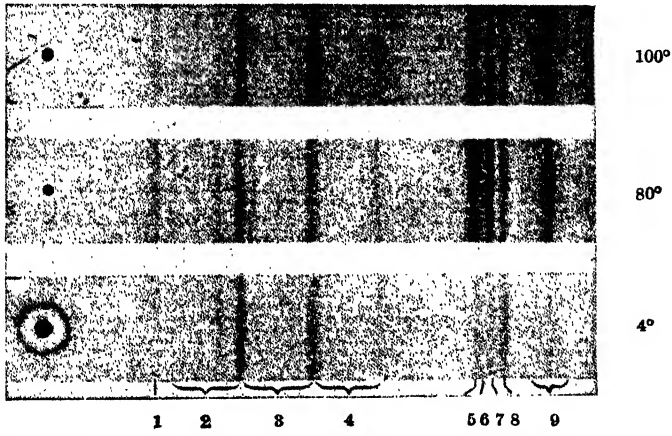


FIG. 11-6.—Magnetic spectrum of photoelectrons ejected at various angles from a thin film of gold. (*Watson and Van den Akker.*) Velocities increase to the right.

1. L_{III} electrons ejected by Mo $K\alpha_{1,2}$.
2. M electrons ejected by Au $L\alpha_1$.
3. M electrons ejected by Au $L\beta_1$.
4. M electrons ejected by Au $L\gamma_1$.
5. M_I electrons ejected by Mo $K\alpha_{1,2}$.
6. M_{II} electrons ejected by Mo $K\alpha_{1,2}$.
7. M_{III} electrons ejected by Mo $K\alpha_{1,2}$.
8. M_{IV} and M_V electrons ejected by Mo $K\alpha_{1,2}$.
9. N and O electrons ejected by Mo $K\alpha_{1,2}$.

Let monochromatic radiation of frequency ν fall upon a thin film of metal. If ν is sufficiently large, then the radiation is capable of ejecting not only those electrons which were initially "free" (the only ones ejected by optical frequencies), but also those which were initially bound to atomic systems. If the energy of binding of the electron to parent atom is W, then after absorption of the incident quantum the electron will emerge with the energy

$$E = h\nu - W.$$

Since for X-ray photoelectrons the relativity correction is of importance, the Einstein equation for this case must be written in the form,

[1] H. ROBINSON, *Proc. Roy. Soc.*, **104**, 455 (1923); *Phil. Mag.*, **50**, 241 (1925); H. ROBINSON and A. M. CASSIE, *Proc. Roy. Soc.*, **113**, 282 (1928); H. ROBINSON and C. L. YOUNG, *Proc. Roy. Soc.*, **128**, 92 (1930).

[2] E. C. WATSON and J. A. VAN DEN AKKER, *Proc. Roy. Soc.* **126**, 138 (1929); *Phys. Rev.*, **37**, 1631 (1931).

$$E = m_0c^2\left(\frac{1}{\sqrt{1-\beta^2}} - 1\right) = h\nu - W, \tag{11-4}$$

where $\beta = v/c$.

Now it is well known that one of the fundamental postulates of the Bohr theory of atomic structure, and all of its more recent modifications, is that, for a given type of atom, W can have only certain discrete values. Thus all electrons ejected from the K energy level of a given atom should emerge with the energy,

$$E_K = h\nu - W_K.$$

Those coming from the L level would have the energy,

$$E_L = h\nu - W_L,$$

etc., where W_K, W_L, etc., are the binding energies for the K, L, . . levels. There will be no electrons of energy intermediate between these two values. Thus a discontinuous velocity distribution of the photoelectrons is a necessary consequence of present theories of atomic structure. The fact that such a distribution is actually observed constitutes possibly the strongest direct evidence for the physical reality of discrete energy levels.

In Fig. 11-6 the various lines have been identified and the origin indicated. The fact that the lines are sharply defined only on the high-velocity[1] side may be attributed to the few energy losses by collision which occur even in thin films of metal. It will be seen that the spectra are in practice considerably complicated by the fact that it is usually not possible to obtain perfectly homogeneous X-rays, and each frequency in the incident radiation produces its own series of photoelectron lines. Furthermore, there are usually a number of fluorescent lines whose origin is to be discussed in the next section.

Now the energy of the ejected photoelectrons can be obtained from the measured deflection in the magnetic field using Eq. 11-3. Hence, if the frequency of the incident radiation is known, the values of W for the various energy levels can at once be computed. This furnishes an independent means for determining the energy values of the X-ray levels of atoms, and in the hands of Robinson and his associates[2] has been made to yield results of high precision. Some of Robinson's results for the photoelectrons ejected from gold have been collected in Table 11-1, from which it can be seen that there is good quantitative agreement between the energy values obtained by the photoelectric method and

[1] This does not show up particularly well on the plate (Fig. 11-6) but may be clearly seen in line 1 of the 80-deg. spectrum.

[2] H. Robinson, *Proc. Roy. Soc.*, **104**, 455 (1923); *Phil. Mag.*, **50**, 241 (1925); H. Robinson and A. M. Cassie, *Proc. Roy. Soc.*, **118**, 282 (1928); H. Robinson and C. L. Young, *Proc. Roy. Soc.*, **128**, 92 (1930).

those deduced from spectroscopic data. (For convenience in making comparison with spectroscopic data Robinson expresses the energy of the incident radiation, of the ejected electrons, and of the energy levels, all in terms of ν/R [ν is the wave-number and R the Rydberg constant] instead of in volts. The Einstein equation can then be written $\frac{\nu_0}{R} = \frac{\nu}{R} - \frac{\nu_1}{R}$; ν_0, ν, and ν_1 referring to the photoelectron, the incident quantum, and the energy level in the atom, respectively. The numbers in the table may be reduced to volts by multiplying by the factor 13.54 [$= 300hcR/e$].) In many cases the photoelectric values are probably more exact than the spectroscopic data.

TABLE 11-1.—VELOCITIES OF PHOTOELECTRONS EJECTED FROM GOLD[1]

Incident X-rays	$\frac{\nu}{R}$	Hr	$\frac{\nu_0}{R}$	Origin	$\frac{\nu_1}{R}$ $\left(= \frac{\nu - \nu_0}{R}\right)$	$\frac{\nu_1}{R}$ (X-ray data)
Mo$K\alpha_1$	1287.8	187.6	229.2	L_{I}	1058.6	1060.2
		205.8	275.6	L_{II}	1012.2	1014.4
		251.2	409.9	L_{III}	877.9	878.5
		401.4	1038.0	M_{I}	249.8	252.9
		405.2	1057.4	M_{II}	230.4	235.1
		411.2	1088.5	M_{III}	199.3	202.8
		418.3	1125.9	M_{IV-V}	161.9	163.0
		440.4	1246.0	N_{I-III}	41.8	41.8
		447.6	1286.4	N, O	1.4	
Mo$K\beta_1$	1444.7	244.0	386.8	L_{I}	1059.2	1060.2
		257.9	431.8	L_{II}	1012.5	1014.2
		296.0	567.9	L_{III}	878.5	878.5
		431.5	1196.0	M_{I}	252.9	252.9
		440.4	1246.0	M_{III}	201.8	202.8
		447.6	1286.4	M_{V}	163.0	163.0
		468.5	1407.2	N_{I-III}	41.8	41.8
Ag$K\alpha_1$	1632.2	298.5	577.5	L_{I}	1054.8	1060.2
		310.0	622.5	L_{II}	1009.8	1014.4
		341.8	755.4	L_{III}	876.9	878.5
		464.9	1386.0	M_{I}	246.3	252.9
		468.0	1404.2	M_{II}	228.1	235.1
		473.1	1434.4	M_{III}	197.9	202.8
		479.5	1472.8	M_{IV-V}	159.5	163.0
		497.0	1580.0	N_{I-II}	52.3	
		498.7	1590.6	N_{III}	41.7	41.8
		501.7	1609.4	N_{V}	22.9	

[1] H. ROBINSON, *Proc. Roy. Soc.*, **104**, 455 (1923); *Phil. Mag.*, **50**, 241 (1925); H. ROBINSON and A. M. CASSIE, *Proc. Roy. Soc.*, **118**, 282 (1928); H. ROBINSON and C. L. YOUNG, *Proc. Roy. Soc.*, **128**, 92 (1930).

As has already been mentioned, a considerable increase in sensitivity and resolving power of the magnetic spectrograph has been obtained by Watson and Van den Akker, using a Geiger-Müller counter in place of a photographic plate to detect the deflected electrons. By this method still more exact values for all the X-ray energy levels may be obtained.

11-4. Multiple Photoelectric Effects.—Magnetic deflection spectra of X-ray photoelectrons have shown that in addition to the electrons ejected by the incident X-ray beam, there are also lines due to electrons ejected by fluorescent radiation excited in the absorbing material.

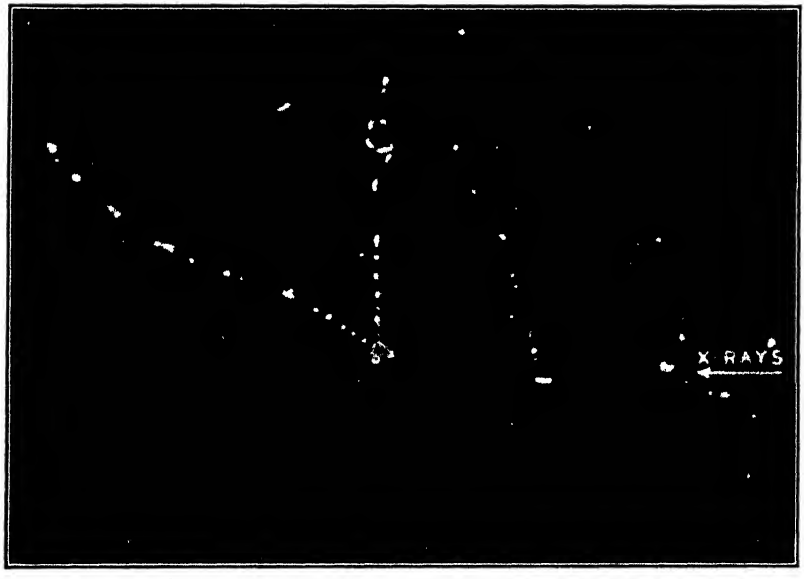


FIG. 11-7.—Photograph of a quadruple photoelectric process. (*Auger.*)

Suppose, for example, that an incident quantum of frequency ν causes the ejection of an electron from the K level of a certain atom. This electron will emerge as a photoelectron with the energy,

$$E_1 = h\nu - W_K = h(\nu - \nu_K),$$

ν_K being the frequency of the K absorption edge of the atom. The vacancy in the K level of the excited atom may now be filled by the transition of an electron from an L level, giving rise to a fluorescent quantum whose frequency is that of the $K\alpha$ line, say $\nu_{K\alpha}$. This quantum, in turn, may cause the ejection of an electron from an L level of the same atom, so that a second photoelectron will emerge having the energy,

$$E_2 = h\nu_{K\alpha} - W_L = h(\nu_{K\alpha} - \nu_L).$$

There are now two vacancies in the L levels of the atom, and these may be filled by transitions from the M or higher levels, giving rise to two more

fluorescent quanta. These may, in turn, eject other photoelectrons from the M or higher levels of the same or neighboring atoms. Thus a single incident quantum might be the cause of the ejection of several photoelectrons of various energies. It is obvious, however, that the total energy of all electrons ejected cannot be greater than that of the incident quantum, and this is found to be the case.[1]

Making use of the cloud expansion chamber, Wilson[2] and Auger[1] have found cases in which as many as three or even four photoelectrons were ejected from the same atom by a single quantum. A photograph of this remarkable phenomenon is reproduced in Fig. 11-7 in which the tracks of two fast and two slow electrons can be seen to emerge from the same point. In the spectrum reproduced in Fig. 11-6 it is seen that a number of the lines are attributed to the electrons ejected by the characteristic lines of the gold film itself, and are referred to as fluorescent lines. A tabulation of some of the fluorescent lines observed by Robinson and his co-workers is given in Table 11-2. It will be seen that the Hr values

TABLE 11-2.—FLUORESCENT ELECTRONS FROM GOLD

Incident X-rays	Hr	ν_0/R	Fluorescent line	Origin	ν_1/R (calc)	ν_1/R (spectroscopic)
Mo K	269.1	470.0	Au L_{α_1}	M_{II}	245.5	234.1
	279.3	506.0	L_{α_1}	M_{III}	209.5	201.8
	280.4	510.0	L_{α_1}	M_{III}	205.5	
	289.5	543.4	L_{α_1}	M_{IV-V}	172.1	163.0 to 169.0
	322.9	674.9	L_{α_1}	N_{1-III}	40.6	5.8 to 58.0
	300.3	584.4	L_{β_1}	M_I	258.6	252.9
	322.9	674.9	L_{β_1}	M_V	168.1	163.0
Ag K	269.1	470.0	L_{α_1}	M_{II}	245.5	
	279.6	507.1	L_{α_1}	M_{III}	208.4	
	289.3	542.7	L_{α_1}	M_{IV}	172.8	
	290.9	548.6	L_{α_1}	M_V	166.9	
	314.4	640.1	L_{β_1}	M_{III}	202.9	
	323.4	677.0	L_{β_1}	M_{IV-V}	166.0	
	335.2	726.8	L_{γ_1}	M_I	259.0	
	348.0	782.8	L_{γ_1}	M_{III}	203.0	
	355.8	817.9	L_{γ_1}	M_{IV-V}	167.9	

for these lines are independent of the nature of the exciting radiation, as would be expected. Furthermore, the values for the energy levels deduced from these lines are in every case somewhat higher than those deduced from spectroscopic data or from a study of the primary photoelectrons. This is at once explained when it is recalled that the electrons con-

[1] P. AUGER, *Comptes Rend.*, **180**, 65 (1925); *Jour. d. Phys. et Rad.*, **6**, 205 (1925).
[2] C. T. R. WILSON, *Proc. Roy. Soc.*, **104**, 192 (1923).

stituting the fluorescent lines have been ejected from atoms which have already lost one deep-lying electron through the action of the incident radiation. The energy levels for such an atom would be expected to be higher than for an unexcited atom. The fact that no fluorescent lines appear showing the unexcited values for the energy levels indicates that the fluorescent quantum ejects the photoelectron from the *same atom* in which it originates, and but seldom from a neighboring unexcited atom.

11-5. The Inverse Photoelectric Effect.—In the photoelectric effect a beam of light or X-rays striking a metal surface causes the emission of electrons whose maximum velocity v_m is given by the Einstein relation,

$$\tfrac{1}{2}mv_m^2 = h\nu - p.$$

If we confine our attention to the case of X-rays where the work function p of the surface may be neglected, and if we measure the maximum velocity of the electrons by determining the opposing potential V required just to stop the fastest ones, this relation takes the form,

$$Ve = h\nu.$$

Now it is well known that a process which is just the inverse of the photoelectric process takes place at the target of an ordinary X-ray tube. For here a beam of electrons of velocity v striking a metal surface causes the emission of radiation. One of the most striking triumphs of the Einstein equation is found in the fact, first discovered by Duane and Hunt,[1] that the maximum frequency of the X-ray beam is given by the relation,

$$h\nu_{max} = \tfrac{1}{2}mv^2 = Ve, \tag{11-5}$$

where V is the potential through which the electrons are accelerated across the X-ray tube. (For high-speed electrons it would, of course, be necessary to use the relativity expression for the kinetic energy in place of $\frac{1}{2}mv^2$.)

The significance of this result is at once apparent. The fact that the Einstein equation can be applied both to the photoelectric effect and its inverse indicates that this relation must express a general law which governs all interactions between electrons and radiation.

The experimental proof of the Duane-Hunt relation was carried out as follows: A crystal X-ray spectrometer with ionization chamber was used to analyze the X-radiation from an ordinary X-ray tube. In general, the X-ray spectrum is known to consist of a continuous background upon which may be superposed one or more lines characteristic of the particular target used. The lines will be absent if the tube is operated at a voltage below that at which these characteristic lines are excited. In this case the continuous spectrum, while extending indef-

[1] W. Duane and F. L. Hunt, *Phys. Rev.*, 6, 166 (1915).

initely to lower frequencies, ceases sharply at an upper frequency limit as shown in Fig. 11-8. The value of ν_{max} is independent of the kind of target used, and depends only on the voltage across the tube. Accurate measurements can be made of ν_{max} and V, and the value of h at once determined.

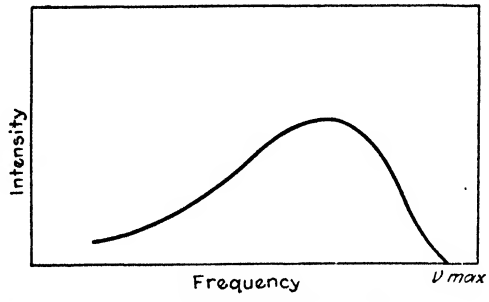


FIG. 11-8.—Typical "continuous" X-ray spectrum.

Another method used was to set the spectrometer to receive X-rays of a definite frequency ν near the maximum. As the voltage across the tube is then lowered, the intensity of the rays of this frequency drops rapidly and vanishes for a certain voltage V_c. V_c and ν are then related

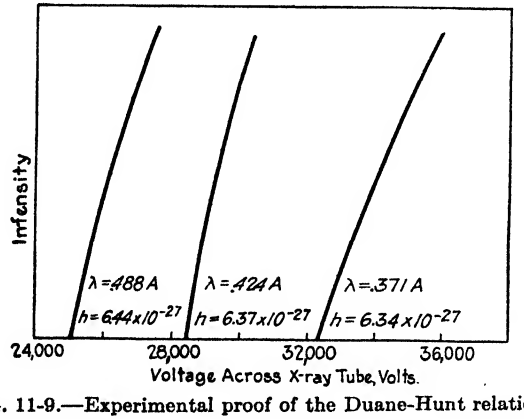


FIG. 11-9.—Experimental proof of the Duane-Hunt relation.

by the Einstein equation. A set of intensity-voltage curves are shown in Fig. 11-9, and it is evident that the extrapolation to zero intensity can be made with considerable precision.

A long series of observations by Duane and his collaborators[1] showed that the values of h, determined from various sets of observations, agreed to within about 0.2 per cent. This is probably the most accurate method

[1] F. L. BLAKE and W. DUANE, *Phys. Rev.*, **10**, 624 (1917); DUANE, PALMER, and CHI SUN YEH, *Jour. Opt. Soc. Amer.*, **5**, 376 (1921).

by which h has been measured, and yields the value, $h = 6.556 \times 10^{-27}$ erg-sec.

11-6. Photoelectrons Ejected by γ-rays.[1]—An extensive study has been made of the extremely high-speed photoelectrons ejected from various materials by γ-rays from radioactive substances.[2] These electrons may attain speeds up to within 0.1 per cent of the velocity of light. Because of their high frequency the γ-rays are capable of ejecting electrons from even the deepest levels of the heaviest atoms, *e.g.*, the K level of uranium. Thus a study of the magnetic spectrum of these so-called "excited" β-rays yields valuable information about atomic energy levels which are beyond the range of ordinary X-ray measurements. Furthermore, it is evident that if the energy of the level from which the electron is ejected be known (from X-ray data), one can, using the Einstein equation, determine the wave-length of the incident γ-rays. Most of the accurate measurements of γ-ray wave-lengths have, in fact, been made by this method.

These excited β-ray spectra have been found for the most part to be line spectra, which means that not only are the electrons ejected from discrete energy levels, but also that the spectrum of the incident γ-rays must be composed of one or more sharply defined lines. Each γ-ray frequency, by ejecting electrons from various energy levels, gives rise to a series of β-ray lines. Table 11-3 gives a typical analysis of a series of β-ray lines, excited in several elements by γ-rays from RaB. All the lines which are here listed can be ascribed to a single γ-ray wave-length, 35.2 X.U. (= 0.0352A).

Results of even greater interest have been obtained from a study of the "natural" β-rays emitted from the radioactive atoms themselves. Following the early work of Baeyer and Hahn,[3] Danysz,[4] and Rutherford and Robinson,[5] the natural β-ray spectra have been extensively studied in recent years by Ellis[6] and Meitner.[7] It has been

[1] For a more extended account of this subject see A. F. Kovarik and L. W. McKeehan, "Report on Radioactivity," *Nat. Research Council Bull.* (1925); also the more recent exhaustive treatment by K. W. F. Kohlrausch, *Handbuch der Experimentalphysik*, Vol. XV (1928).

[2] E. Rutherford and E. N. da C. Andrade, *Phil. Mag.*, **27**, 854 (1914); C. D. Ellis, *Proc. Roy. Soc.*, **100**, 1 (1922); C. D. Ellis and H. W. B. Skinner, *Proc. Roy. Soc.*, **105**, 185 (1924); L. Meitner, *Zeits. f. Phys.*, **9**, 131 (1922); M. de Broglie and J. Cabrera, *Comptes Rend.*, **176**, 295 (1923); J. Thibaud, *Comptes Rend.*, **178**, 1706 (1924); D. H. Black, *Proc. Roy. Soc.*, **106**, 632 (1924).

[3] O. v. Baeyer and O. Hahn, *Phys. Zeits.*, **11**, 488 (1910).

[4] J. Danysz, *Le Radium*, **10**, 4 (1913); *Ann. d. Chim. et Phys.*, **30**, 241 (1913); *Comptes Rend.*, **153**, 1066 (1911).

[5] E. Rutherford and H. R. Robinson, *Phil. Mag.*, **26**, 717 (1913); **28**, 552 (1914).

[6] C. D. Ellis, *Proc. Roy. Soc.*, **99**, 261 (1921); **100**, 1 (1922); Ellis and Skinner, *Proc. Roy. Soc.*, **105**, 60, 165, and 185 (1924).

[7] L. Meitner, *Zeits. f. Phys.*, **9**, 131 (1922); **17**, 54 (1923); **11**, 35 (1922).

TABLE 11-3.*—ANALYSIS OF EXCITED β-RAYS.

I	II	III	IV	V	VI
Origin	V_β kv	V_i kv	$h\nu/e$ kv	λ X-units	References
Pt, K	265	78	343	35.9	1
	269	78	347	35.5	2
	275	78	353	34.9	3
Pt, L_{III}	340	12	352	35.0	3
Pt, M	352	3	355	34.7	3
W, K	276	69	345	35.7	2
Pb, K	258	87	345	35.7	1
	260	87	347	35.5	2
	261	87	348	35.4	2
	264	87	351	35.1	3
	265	87	352	35.0	3
Pb, L_I	333	16	349	35.4	2
Pb, L_{III}	338	13	351	35.2	3
Pb, M	350.2	3.2	353.4	34.9	3
Pb, N	353.6	0.5	354.1	34.8	3
U, K	231	115	346	35.6	2
	238	115	353	34.9	1

KEY TO TABLE

I. Atomic level from which photoelectron (β-ray) was ejected.

II. Energy of β-ray in kilovolts.

III. Energy of level listed in column I.

IV. Energy $h\nu/e$ of incident quantum, computed from Einstein equation $h\nu/e = V_\beta + V_i$.

V. Wave-length of incident quantum, $\lambda = c/\nu$.

[1] DE BROGLIE and CABRERA, *Comptes Rend.*, **176**, 295, 1923.

[2] ELLIS, *Proc. Roy. Soc.*, **99**, 261, 1921.

[3] ELLIS and SKINNER, *Proc. Roy. Soc.*, **105**, 165, 1924.

* Taken from a complete tabulation of β-ray spectra given by Kovarik and McKeehan, "Report on Radioactivity," *Nat. Research Council Bull.*

found that the velocity spectra of these rays consist also, in general, of a number of sharply defined lines, superposed on a continuous background.[1] The continuous background seems to be due to β-rays ejected from the nucleus of the atom. Analysis of the *lines* has shown that most if not all of them are due to β-rays ejected, not from the nucleus, but from the deeper X-ray levels. They are, in fact, *photoelectrons* ejected from the atom by the primary γ-rays. The photoelectric process thus plays a rôle of primary importance in the study of radioactivity. By using the Einstein equation the frequency of the primary γ-rays can at once be computed. The results confirm those deduced from the excited β-ray spectra, namely that the γ-ray spectra are line spectra.

[1] J. CHADWICK, *Verh. d. Deutsch. Phys. Ges.*, **16**, 383 (1914); A. F. KOVARIK and L. W. MCKEEHAN, *Phys. Rev.*, **8**, 574 (1916).

A study of the γ-ray spectra[1] obtained by analysis of β-ray velocities has yielded at least two results of fundamental importance:

1. Many of the γ-ray frequencies have been found to be identical with the frequencies of the K, L, and M X-ray frequencies of the radioactive atom concerned. This means that many of the γ-rays therefore are not of nuclear origin, but are simply fluorescent X-rays, excited in the lower levels of the atom by the primary β- or γ-rays from the nucleus.

2. Some of the γ-ray lines, however, because of their extremely high frequencies, cannot be accounted for in this manner and must have originated in the nucleus. Since these too constitute a line spectrum, this furnishes strong evidence for the existence of discrete energy levels within the nucleus itself, similar to those known to exist in the surrounding electron structure.

11-7. Spatial Distribution of Photoelectrons.—One of the most interesting questions in the whole field of photoelectricity relates to the directional distribution of the initial velocities of photoelectrons. In the case of electrons ejected from metals by ultra-violet light, the initial direction of the electron velocity is largely obliterated by the time it leaves the surface. Only a beginning has been made[2] in the study of the direction of electrons ejected by ultra-violet light from atoms of a gas. In the case of X-rays, however, the Wilson expansion-chamber method allows direct observation of the initial direction of ejection of each individual photoelectron and an extensive experimental and theoretical study of this problem has been made. The experimental method involves merely the making of stereoscopic photographs of the electron tracks, from which their direction in space may be determined. From observations on a large number of tracks the spatial distribution curves may be plotted. Quite recently Watson and Van den Akker[3] have developed a method by which, using the magnetic spectrograph, a study may be made of the distribution in direction of each type of photoelectron, *e.g.*, K, L_{I}, L_{II}, etc. By this method important differences in the spatial distribution of the L_{I}, L_{II}, and L_{III} electrons have been observed, though the tracks of these electrons are indistinguishable in the expansion chamber. A third method of investigation has been used by Bothe,[4] in which a movable Geiger counter was used to count

[1] A complete tabulation of γ-ray spectra has been given by Kovarik and McKeehan, "Report on Radioactivity," *Nat. Research Council Bull.* A study of the γ-ray spectrum of radium has recently been made by the method of crystal reflection by L. T. Steadman, *Phys. Rev.*, **36**, 460 (1930).

[2] E. O. Lawrence and M. A. Chaffee, *Phys. Rev.*, **36**, 1099 (1930). M. A. Chaffee, *Phys. Rev.*, **37**, 1233 (1931).

[3] E. C. Watson and J. A. Van den Akker, *Proc. Roy. Soc.*, **126**, 138 (1929).

[4] W. Bothe, *Zeits. f. Phys.*, **26**, 59 (1924).

the number of electrons ejected at different angles with reference to the X-ray beam.

Two different types of distribution curves have been studied. In the first, the "longitudinal" distribution, measurements are made of the angle θ between the initial direction of the photoelectron and the direction of the incident X-ray beam. The number of electrons ejected within a given angular range is then plotted as a function of this angle. In order that there shall be symmetry about the direction of the X-ray beam, unpolarized rays are used. In the second or "lateral" type of distribution, polarized X-rays are used and a study is made of the directional distribution of the *components* of the electron velocity which lie *in a plane* at right angles to the direction of the beam.

Interest in the longitudinal distribution of the photoelectrons was first aroused by the observations of Beatty,[1] Cooksey,[2] and others,[3] that, when X-rays were allowed to pass through thin films of metal, a considerably greater number of photoelectrons were ejected from the emergent than from the incident side of the film. A similar asymmetry in the distribution of the β-rays (photoelectrons) ejected from metal foil by γ-rays from radium had previously been established by the work of Bragg and Madsen.[4] This asymmetry[5] was found to increase with increasing frequency of the incident radiation, the ratio of the number of emergent to the number of incident electrons being as high as 20 for γ-rays and decreasing to very nearly unity for soft X-rays.

The first quantitative studies of the longitudinal distribution were made by Bothe,[6] who passed a beam of X-rays through a chamber containing a gas or vapor and observed with a Geiger counter the number of electrons ejected in various directions. During recent years an extensive study of this problem has been made by the expansion-chamber method, principally by Auger,[7] Loughridge,[8] and Anderson,[9] and Williams, Nuttall, and Barlow.[10] A typical distribution curve

[1] R. T. Beatty, *Proc. Camb. Phil. Soc.*, **15**, 492 (1910).

[2] C. D. Cooksey, *Phil. Mag.*, **24**, 37 (1912).

[3] W. H. Bragg and H. L. Porter, *Proc. Roy. Soc.*, **85**, 355 (1911).

[4] W. H. Bragg and J. P. V. Madsen, *Phil. Mag.*, **16**, 918 (1908); **17**, 423 (1909).

[5] An asymmetry discovered by Stuhlmann for the photoelectrons ejected by ultra-violet light from thin films of metal mounted on quartz plates was later explained by Partzsch and Hallwachs as due to the difference in the reflecting power of the two surfaces of the film. Hence it is not an effect of the type considered here (see page 122).

[6] W. Bothe, *Zeits. f. Phys.*, **26**, 59 (1924).

[7] P. Auger, *Comptes Rend.*, **187**, 1141 (1928); *Jour. d. Physique*, **9**, 225 (1928).

[8] D. H. Loughridge, *Phys. Rev.*, **30**, 488 (1927).

[9] C. D. Anderson, *Phys. Rev.*, **34**, 547 (1929); **35**, 1139 (1930).

[10] E. J. Williams, J. M. Nuttall, and H. S. Barlow, *Proc. Roy. Soc.*, **121**, 611 (1928).

obtained by Auger is reproduced in Fig. 11-10, plotted in polar coordinates, and in Fig. 11-11 are shown curves recently obtained by Anderson. It will be seen at once that most of the photoelectrons are ejected in directions nearly at right angles to the direction of the incident beam, though in each case the *most probable* direction of ejection is definitely

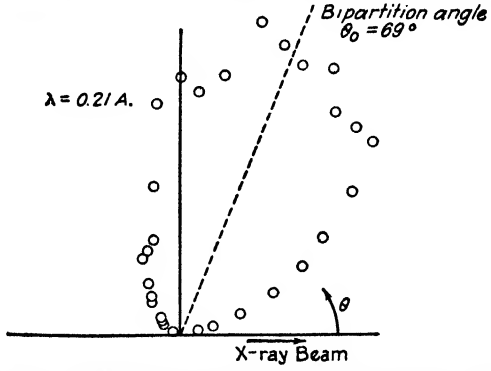


FIG. 11-10.—Longitudinal distribution of 1,000 photoelectrons ejected from argon by W$K\alpha$ X-rays. (*Auger.*)

forward of 90 deg. This forward component increases with increasing frequency of the incident beam and accounts for the asymmetry observed with electrons ejected from thin films.

The main features of these longitudinal-distribution curves may be understood from a simple view of the photoelectric process. The tend-

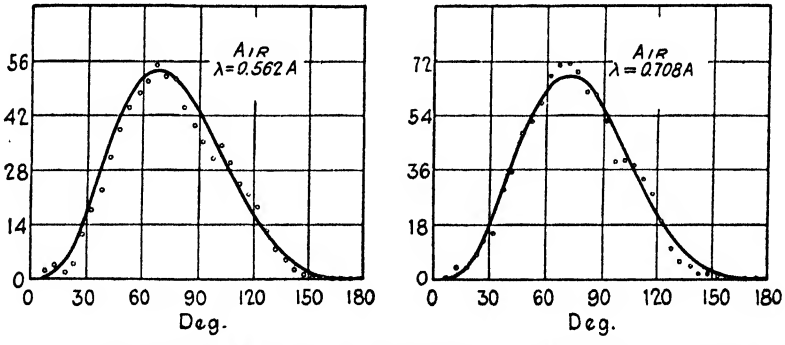


FIG. 11-11.—Longitudinal distribution of photoelectrons. (*Anderson.*) The solid curves represent the theoretical distribution deduced by Wentzel (Sec. **11-9**).

ency of the electrons to be ejected principally in directions at right angles to the X-ray beam is attributed to the fact that the electron receives its initial impulse in the direction of the electric vector of the radiation. The forward component is due to the fact that the photoelectron receives not only the energy but also the momentum of the incident quantum. Since the momentum of the quantum is $h\nu/c$ it would be expected that the forward component of the electron velocity would increase with

increasing frequency, as observed.[1] The experiments have not been in agreement, however, as to the actual magnitude of the asymmetry in the longitudinal distribution. As a measure of the asymmetry it is customary to use the "bipartition angle," which is the half-angle of the cone which contains half of all the emitted electrons. For a distribution perfectly symmetrical about the electric vector, the bipartition angle would be equal to 90 deg. The actual curves obtained by various observers show values for this angle ranging from about 60 to 85 deg, the angle in general increasing with the wave-length of the incident radiation and with the atomic number of the atom from which the electrons are ejected. However, there is a lack of quantitative agreement between the results of different observers. The most recent precise results of Williams, Nuttall, and Barlow, of Auger, and of Anderson, give values for this angle which are definitely smaller than those obtained previously.[1] The average forward component of the momentum of the electrons is found to be greater than the value of $h\nu/c$ predicted by the simple corpuscular theory of the process, but in good agreement with value predicted by wave-mechanical theory to be discussed in Sec. **11-9**.

Studies of the *lateral* distribution of the initial directions of photoelectrons have been made with the expansion-chamber method, principally by Bubb[2] and Kirchner.[3] In each case the X-rays were polarized before entering the chamber by scattering at 90 deg from a block of paraffin. The scattered rays thus obtained are about 80 per cent polarized and correction could be made for the lack of complete polarization. The axis of the camera in these experiments is parallel to the direction of the X-ray beam, instead of at right angles to it, as in the experiments on the longitudinal distribution.

If φ is the angle between the initial direction of the electron track and the direction of the electric vector, then plotting the number of electrons ejected in the angular range $\delta\varphi$ as a function of φ on a polar diagram, Bubb obtained the curve shown in Fig. 11-12. It will be noted that there is a marked concentration in the direction of the electric vector, the few electrons ejected at right angles to the electric vector being accounted for by the lack of complete polarization. These results were confirmed by Kirchner who, in a more extensive series of measurements, showed also that the form of the distribution curve is independent of the frequency of the incident X-rays and of the nature of the gas atoms from which the photoelectrons are ejected. He has shown further that the number of electrons ejected at the angle φ is

[1] Particularly by W. Bothe, *Zeits. f. Phys.*, **26**, 59 (1924).

[2] F. W. Bubb, *Phys. Rev.*, **23**, 137 (1924).

[3] F. Kirchner, *Phys. Zeits.*, **27**, 799 (1926); *Ann. d. Phys.*, **81**, 1113 (1926); **83**, 521 (1927).

closely proportional to $\cos^2 \varphi$. In Fig. 11-13[1] the results of Bubb and Kirchner are plotted in an integral form in which the ordinate at any angle, say φ_1, represents the total number of electrons ejected in the range $\varphi = 90$ deg to $\varphi = \varphi_1$. By this method of plotting the statistical variations are minimized. The ordinates of the solid curve are proportional to $\int \cos^2 \varphi \, d\varphi$ and it is seen that the experimental points fall very close to this curve. Similar results have been obtained by Pietenpol.[2] The view is thus confirmed that the number of electrons ejected in any direction in a plane perpendicular to the X-ray beam is proportional to the square of the component of the electric vector in that direction. Since this distribution is independent of the frequency of the incident radiation, it would be expected to hold also for the initial direction of ejection of electrons within a metal illuminated by ultra-violet light, an assumption which seems necessary to explain the selective photoelectric effect (see Chapter V).

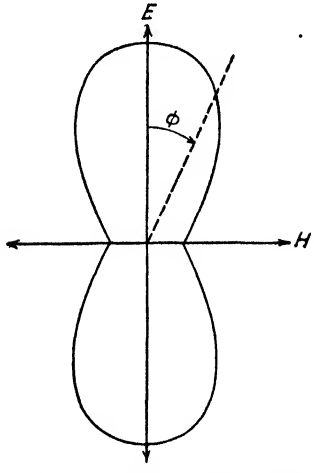


FIG. 11-12.—Lateral distribution of photoelectrons ejected in air. (*Bubb.*)

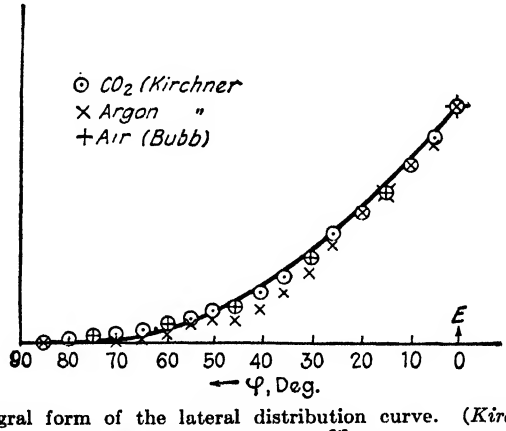


FIG. 11-13.—Integral form of the lateral distribution curve. (*Kirchner.*) The curve represents the expression $\int_{90}^{\varphi} \cos^2 \varphi \, d\varphi$.

11-8. Corpuscular Theory of the Photoelectric Process.—Since in the Wilson expansion chamber one can observe directly the expulsion of a photoelectron from an atom, it is of interest to consider more in detail the simple corpuscular theory of this process, given by Compton.[3]

[1] Taken from F. Kirchner, *Handbuch der Experimentalphysik*, Vol. XXIV, p. 202.

[2] C. S. PIETENPOL, *Phys. Rev.*, **32**, 564 (1928).

[3] A. H. COMPTON, "X-rays and Electrons," pp. 240–246.

The theory applies the principles of conservation of energy and momentum to the collision between a quantum and an electron within an atom. It is assumed that electron and atom are initially at rest, and that the energy required to remove the electron from the atom is negligible. From the conservation of energy we have,

$$h\nu = mc^2\left(\frac{1}{\sqrt{1-\beta^2}} - 1\right) + \frac{1}{2}MV^2 \tag{11-6}$$

where βc is the final speed of the electron, V the speed of the remainder of the atom, m the "rest mass" of the electron, and M the mass of the atom. Since the momentum of the incident quantum is $h\nu/c$, and since it is evident that all the paths will lie in the same plane, we have the two momentum equations,

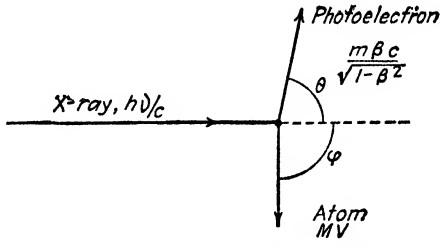


FIG. 11-14.—Momentum diagram for an elementary photoelectric process.

$$\frac{h\nu}{c} = \frac{m\beta c \cos\theta}{\sqrt{1-\beta^2}} + MV\cos\varphi, \tag{11-7}$$

$$0 = \frac{m\beta c \sin\theta}{\sqrt{1-\beta^2}} - MV\sin\varphi, \tag{11-8}$$

where θ and φ are the angles made by the paths of the electron and atom, respectively, with the direction of the incident quantum as shown in Fig. 11-14.

The further assumption is made that the impulse given to the *atom*[1] is in the direction of the electric vector of the polarized X-ray beam, *i.e.*, that

$$\varphi = \frac{\pi}{2},\ \cos\varphi = 0,\ \sin\varphi = 1.$$

Equation (11-8) then becomes,

$$\frac{m\beta c}{\sqrt{1-\beta^2}} = \frac{MV}{\sin\theta}, \tag{11-9}$$

[1] The essential rôle played by the atom in the photoelectric process is seen if we attempt to apply conservation of energy and momentum to the collision between quantum and free electron. We have then, neglecting relativity corrections,

$$h\nu = \tfrac{1}{2}mv^2$$

$$\frac{h\nu}{c} = mv.$$

Hence we would have, $v = 2c$, which is impossible. Hence there must be a third body involved. See page 193.

which means that the momentum of the electron is greater than, but of the same order of magnitude as, the momentum of the atom. Hence the kinetic energy of the electron will be greater than that of the atom in the ratio ($M/m \sin \theta$), a number which will be of the order of 10^4. Therefore in Eq. (11-6) we may neglect the term $\frac{1}{2}MV^2$ and write,

$$h\nu = mc^2\left[\frac{1}{\sqrt{1-\beta^2}} - 1\right], \tag{11-10}$$

which is the Einstein equation.

Calling the momentum of the electron p, then

$$p = \frac{m\beta c}{\sqrt{(1-\beta^2)}}, \tag{11-11}$$

from which it follows,

$$\frac{1}{(1-\beta^2)} = 1 + \frac{p^2}{m^2c^2} = 1 + b^2, \tag{11-12}$$

where we have set $b = p/mc$. From Eq. (11-10) it follows that

$$\frac{1}{\sqrt{(1-\beta^2)}} = 1 + \alpha, \tag{11-13}$$

where $\alpha = h\nu/mc^2$. Combining Eqs. (11-12) and (11-13), we obtain the relation,

$$b^2 = 2\alpha + \alpha^2. \tag{11-14}$$

Now from Eq. (11-7) we have, since $\cos \varphi = 0$,

$$\cos \theta = \frac{h\nu}{pc},$$

which to first order terms reduces to

$$\cos \theta = \tfrac{1}{2}\beta. \tag{11-15}$$

Or, using Eq. 11-14,

$$\cos \theta = \frac{\alpha}{b} = \frac{1}{\sqrt{\left(1 + \frac{2}{\alpha}\right)}}.$$

Hence,

$$\tan \theta = \sqrt{\left(\frac{2}{\alpha}\right)}. \tag{11-16}$$

From this expression the direction of ejection of the electron may be computed for incident X-rays of any wave-length. In the computation it is convenient to set

$$\alpha = \frac{\gamma}{\lambda},$$

where

$$\gamma = \frac{h}{mc} = 0.0243\text{A}. \tag{11-17}$$

Values of θ for a series of values of λ are recorded in Table 11-4. It will be noted that it is only for frequencies greater than those correspond-

TABLE 11-4.—THEORETICAL EMISSION ANGLES FOR PHOTOELECTRONS*

λ A.u.	θ
0.0243	55°
0.243	76°27′
2.43	85°58′
24.3	88°43′
243.	89°36′
2430.	89°52′

* A. H. Compton, "X-rays and Electrons, pp. 240–246.

ing to soft X-rays that an appreciable forward component is to be expected. While the longitudinal distribution curves discussed in the previous section show a forward component in qualitative agreement with the values in the table, it has been found that this simple theory is incapable of giving a satisfactory account of the "spread" of the distribution curves. Furthermore, recent results have shown a forward component definitely greater than that computed from Eq. (11-15). The theory, nevertheless, gives a simple and often useful physical picture of the photoelectric process.

11-9. Wave-mechanical Theory.—Wentzel[1] and Beck[2] have, on the basis of the wave mechanics, developed a theory of the photoelectric effect which accounts quantitatively not only for the velocity of emission, but also for the spatial distribution of the photoelectrons ejected from atoms by light or X-rays. The theory has been reviewed and extended by Sommerfeld[3] and we shall state only the conclusions which have been reached.

The theory starts out by considering the perturbation of a hydrogen atom by a beam of radiation whose wave-length is large compared to the dimensions of the atom. The mathematical methods are similar to those used in the theory of dispersion, the distinction lying in the fact that, in the dispersion theory, perturbations of the discrete levels only are considered, while in the theory of the photoelectric effect only the

[1] G. WENTZEL, *Zeits. f. Phys.*, **40**, 574 (1926); **41**, 828 (1927).
[2] G. BECK, *Zeits. f. Phys.*, **41**, 443 (1927).
[3] A. SOMMERFELD, "Wave Mechanics," p. 177 (English edition, Methuen, 1930).

continuous levels are involved. It is found that the perturbed *Eigenfunktion* may be reduced to the form,

$$\frac{C}{r} \cos \varphi \, e^{i(kr+a)} e^{\left(\frac{2\pi i}{h}\right)(h\nu - J)t}, \tag{11-18}$$

C and k being constants, a being an abbreviation for $B \log r$, where B is a constant, and J is the ionization energy of the atom. The angle φ, as before, is measured from the direction of the electric vector. This function is interpreted as representing a spherical wave (electron wave) moving in the positive direction of r (away from the atom) and having the energy $(h\nu - J)$. This means simply that an electron may be ejected from the atom with an energy given by the Einstein equation. The probability of emergence in the direction φ is proportional to the square of the coefficient of the time factor, and hence to $\cos^2 \varphi$. The directional distribution in any plane containing the electric vector should thus be proportional to $\cos^2 \varphi$, so that the distribution in space would be represented by the $\cos^2 \varphi$ curve shown in Fig. 11-15 rotated about its vertical axis. It is at once evident that this distribution is in agreement with the experimental results for the lateral distribution. In plotting longitudinal distribution curves, however, it is usual to plot not the distribution of directions in a plane, but the total number of electrons making an angle θ in the range $d\theta$ with the direction of the incident beam. This would be the number emitted in a cone between the angles θ and $\theta + d\theta$, and would thus be proportional to $\sin^3 \theta$. The longitudinal distribution for long wave-lengths should be of this form, and would show a maximum in the direction of the electric vector.

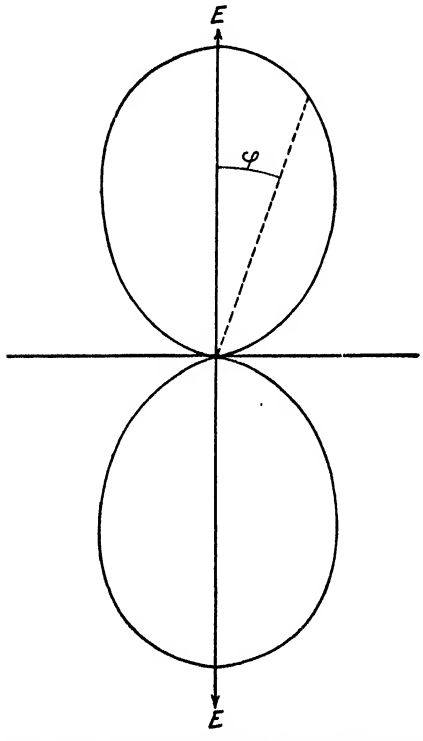


FIG. 11-15.—Theoretical $\cos^2 \varphi$ distribution law.

However, for X-rays the assumption that the wave-length is large compared to the dimensions of the atom no longer holds, and the simple treatment must be modified. Sommerfeld has carried out this extension

for the case of the hydrogen atom, and finds that the bipartition angle of the electron distribution no longer has the value $\theta_0 = \pi/2$, but is displaced forward to an angle θ_0, such that, to a first approximation,

$$\cos \theta_0 = \beta.$$

It will be noted that this value for $\cos \theta_0$ is just twice that given by Eq. (11-15), derived on the simple corpuscular theory of the process. The wave mechanics thus predicts a greater forward component than that predicted by the older theory, and is in quantitative agreement with the recent accurate measurements of Auger,[1] Anderson,[2] and Williams,

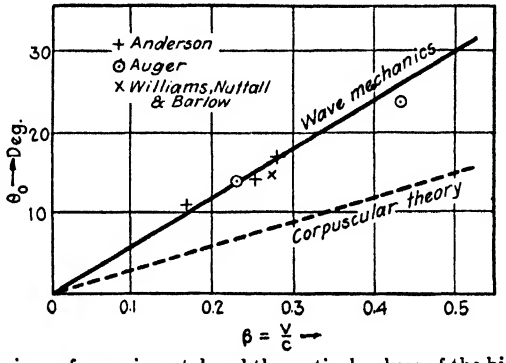


FIG. 11-16.—Comparison of experimental and theoretical values of the bi partition angle, θ_0.

Nuttall, and Barlow.[3] A comparison of theoretical and experimental values is shown in Fig. 11-16.

While this simple theory refers only to the hydrogen atom, it may be at once generalized to apply to the K level of any atom. Wentzel[4] gives the following expression for the value of $P(\theta)d\theta$, the probability that a photoelectron from a K level will emerge at the angle θ, in the range $d\theta$,

$$P(\theta)d\theta = \frac{\sin^3 \theta \, d\theta}{\left(1 - \beta \cos \theta + \frac{\alpha}{2}\right)^4}, \tag{11-19}$$

where, as before, $\alpha = h\nu/mc^2$. Anderson has made a direct comparison of this expression with his experimental results, and in the curves reproduced in Fig. 11-11 the solid lines represent the computed curves. The agreement with the experimental points is well within the errors due to statistical fluctuations. The computed values of the bipartition angle are also in excellent agreement with experiment.

[1] P. AUGER, *Comptes Rend.*, **188**, 447 (1929).

[2] C. D. ANDERSON, *Phys. Rev.*, **34**, 547 (1929); **35**, 1139 (1930).

[3] E. J. WILLIAMS, J. M. NUTTALL, and H. S. BARLOW, *Proc. Roy. Soc.*, **121**, 611 (1928).

[4] G. WENTZEL, "Pasadena Lectures," quoted by C. D. Anderson, *loc. cit.*

An expression for the longitudinal distribution of the L electrons has been derived by Schur,[1] and Anderson has also found it to be in "fair accord" with his results. The distribution for the L electrons is considerably more isotropic than for the K electrons, a conclusion which had also been reached by Watson and Van den Akker[2] from their experiments with the magnetic spectrograph. In no other experiments have the K and L electrons been studied separately.

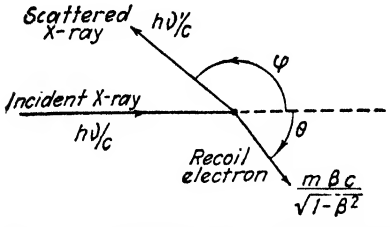


FIG. 11-17.—Momentum diagram for Compton process.

11-10. The Compton Effect.—In Sec. **11-8** we applied the principles of conservation of energy and momentum to the collision between a quantum and a bound electron. If we attempt to apply these principles to the collision between a quantum and a free electron, simple considerations show at once that it is impossible to satisfy them unless a third body is involved. Hence such an encounter must give rise also to a scattered quantum of some frequency, ν'. The equations for conservation of energy and momentum may now be written (see Fig. 11-17),

$$h\nu = h\nu' + mc^2\left[\frac{1}{\sqrt{1-\beta^2}} - 1\right], \tag{11-20}$$

$$\frac{h\nu}{c} = \frac{h\nu'}{c}\cos\varphi + \frac{m\beta c\cos\theta}{\sqrt{1-\beta^2}}, \tag{11-21}$$

$$0 = \frac{h\nu'}{c}\sin\varphi - \frac{m\beta c\sin\theta}{\sqrt{1-\beta^2}}. \tag{11-22}$$

By a straightforward solution of these equations, eliminating θ and making the substitutions $\lambda = c/\nu$ and $\lambda' = c/\nu'$, we obtain the well-known equation for the Compton effect,

$$\lambda' - \lambda = \left(\frac{h}{mc}\right)(1 - \cos\varphi). \tag{11-23}$$

The relation between the angle of scattering φ and the angle of ejection of the recoil electron θ is given by

$$\tan\tfrac{1}{2}\varphi = \frac{-1}{(1+\alpha)\tan\theta}. \tag{11-24}$$

For a given angle of scattering, the change in wave-length is thus independent of the frequency of the incident beam, and for the particular case of $\varphi = \pi/2$ we have,

[1] G. SCHUR, *Ann. d. Phys.*, **4**, 441 (1930).

[2] E. C. WATSON and J. A. VAN DEN AKKER, *Proc. Roy. Soc.*, **126**, 138 (1929).

$$\lambda' - \lambda = \frac{h}{mc} = 0.0242\text{A}.$$

The experimental proof of the existence of scattered radiation of smaller frequency than the primary was obtained by J. A. Gray and A. H. Compton.[1] On scattering monochromatic X-rays from various materials, Compton found that the spectrum of the scattered radiation showed the existence of a modified as well as the unmodified line. The wave-length difference between the two lines was very closely that given by the above simple theory, and showed the expected variation with angle of scattering, φ. This result, which has since been repeatedly verified by other observers, undoubtedly constitutes one of the most important triumphs for the pure corpuscular theory of radiation.

In the Compton experiments no attempt was made to detect the recoil electrons which should be ejected from the scattering material with a kinetic energy given by

$$E = h\nu - h\nu'. \tag{11-25}$$

However, shortly after the discovery of the Compton effect, C. T. R. Wilson[2] and Bothe[3] independently announced the discovery, in expansion-chamber photographs, of the tracks of the recoil electrons. Since these electrons absorb only a small fraction of the energy of the incident quanta, their tracks are easily distinguishable by their shortness from the much longer tracks of the photoelectrons. Several tracks of this type may be seen in the photograph reproduced in Fig. 11-3. They were called by Wilson "fish-tracks." As nearly as can be determined, the lengths of these tracks are about what would be expected on computing their energy from Eq. (11-20), and those which lie most nearly in the direction of the incident beam are the longest, as expected.

It is evident that while the Compton effect and the photoelectric effect are closely related, there is, nevertheless, an important distinction between them. Referring to the simple theory of the two processes which has been given above, it is seen that this distinction lies in the fact that in the Compton process only the quantum and electron are involved, while in the photoelectric effect a third body of large mass takes part in the encounter. It is the presence of this third body, *e.g.*, the atom, which makes it possible for the photoelectron to absorb *all* of the energy of the incident quantum, while the recoil electron absorbs only a fraction thereof. This distinction between the two effects is sometimes interpreted as meaning that *only* free electrons can become recoil electrons and only bound electrons become photoelectrons. This statement is not strictly true, and requires interpretation as to what is meant by *free* and *bound*. It is true that a perfectly free electron, such as would be found in the electron atmosphere surrounding a hot filament in vacuum, could absorb energy from

[1] J. A. Gray, *Phil. Mag.*, **26**, 611 (1913); A. H. Compton, *Phys. Rev.*, **21**, 715 (1923); "X-rays and Electrons," pp. 240–246.

[2] C. T. R. Wilson, *Proc. Roy. Soc.*, **104**, 1 (1923).

[3] W. Bothe, *Zeits. f. Phys.*, **16**, 319 (1923); **20**, 237 (1923).

incident radiation *only* by the Compton process. But such an effect has never been observed. The *so-called "free"* or conduction electrons within a metal are not free in this sense, since they are bound to the block of metal which may itself play the rôle of the third body of mass M. Such electrons may then absorb energy by *either* the photoelectric or Compton processes. Similarly, electrons loosely bound to atomic systems may also take part in either type of encounter, as is often observed when X-rays pass through the atmosphere of an expansion chamber. In order to be ejected as recoil electrons it is only necessary that the energy they absorb from the radiation be greater than that required to free them from the atom. Electrons too tightly bound to be freed by a Compton process might still be freed by the photoelectric action of the same radiation. This question has been discussed from a different viewpoint in Sec. **6-8**.

It is of interest to compute the fraction of the energy of the incident quantum which can be absorbed by a recoil electron in a Compton process. Calling this fraction f, it is evident from Eq. (11-25) that,

$$f = \frac{(\nu - \nu')}{\nu}.$$

From Eq. (11-23) it may at once be shown that

$$f = \frac{\alpha(1 - \cos\varphi)}{(1 + \alpha[1 - \cos\varphi])},$$

where we have set $\alpha = h\nu/mc^2$ as before. Taking the angle of scattering, φ, as 90 deg, for example, this becomes

$$f_{90} = \frac{\alpha}{(1 + \alpha)}. \tag{11-26}$$

Values of f_{90} for a number of values of the incident wave-length are tabulated in Table 11-5. As ν varies from 0 to infinity, f_{90} varies from 0 to 1, and has an appreciable value only for frequencies higher than those corresponding to soft X-rays. For cosmic rays, on the other hand, f is nearly unity, which means that the energy of a recoil electron will be nearly as great as that of the fastest photoelectrons ejected by the same radiation.

TABLE 11-5.—RELATIVE ENERGY OF RECOIL ELECTRONS FOR 90-DEG SCATTERING

λ, A. u.	$f_{90} = (\nu - \nu')/\nu$	Type of radiation
2430	10^{-5}	Ultra-violet
243	10^{-4}	Extreme ultra-violet
24.3	10^{-3}	
2.41	10^{-2}	Soft X-rays
0.219	0.1	Hard X-rays
0.0243	0.5	γ-rays
0.00243	0.91	
0.0002	0.99	Cosmic rays

The recently discovered Raman effect is closely related to the Compton effect in that it involves a scattering with change of wave-length of visible or ultra-violet light. In this case, however, the energy lost by the radiation goes to *excite* rather than to ionize an atom or molecule of the scattering substance. The incident quantum may also receive energy from an already excited atom, and thus be scattered with increase in frequency—a phenomenon impossible in Compton scattering. Since the Raman effect involves merely the excitation of an atom and not the ejection of an electron, it does not come under the head of photoelectric processes with which we are concerned in this book.

11-11. Spatial Distribution of Recoil Electrons.—A direct test of the assumption that energy and momentum are conserved in each individual scattering process has been made by Compton and Simon,[1] using the Wilson expansion chamber. These observers found that occasionally a quantum, after scattering by a Compton process, might cause the ejection of a photoelectron at some distance from the primary X-ray beam. A number of photographs of such double processes were actually obtained, similar to the diagram shown in Fig. 11-18. From the initial direction of the path of the recoil electron, the direction of its ejection, θ, may be determined. By drawing a line from the point where the recoil electron starts to where the photoelectron is ejected, the path of the scattered quantum is obtained and the angle of scattering, φ, is determined. According to the simple theory of the process these two angles should be related by the equation,

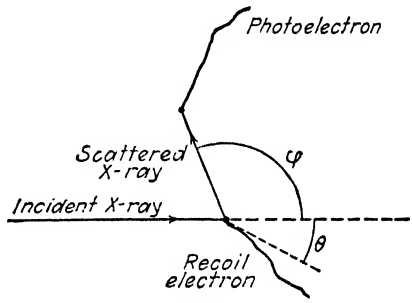


FIG. 11-18.—Diagram of electron tracks showing ejection of recoil electron and photoelectron. (*Compton and Simon.*)

$$\tan \tfrac{1}{2}\varphi = \frac{-1}{(1 + \alpha) \tan \theta}, \tag{11-24}$$

where $\alpha = h\nu/mc^2$. This relation was found to hold within the limits of experimental error. This means clearly that conservation of energy and momentum are not merely statistical laws but may be applied to each individual encounter.

An examination of Eq. (11-24) shows that as the angle of scattering, φ, increases from 0 to 180 deg, θ increases from -90 to 0 deg (Fig. 11-18). Thus all the recoil electrons should be ejected within an angle of less than 90 deg with the incident beam, as is observed. An expression for the longitudinal distribution of the recoil electrons ejected by X-rays

[1] A. H. COMPTON and A. W. SIMON, *Proc. Nat. Acad. Sci.*, **11**, 303 (1925); *Phys. Rev.*, **26**, 289 (1925).

has been calculated by Compton and Hubbard,[1] and by Jauncey,[2] according to which *most* of the observable recoil-electron tracks should make an angle of less than 45 deg with the incident beam.[3] This is in general agreement with observation, though no quantitative study of the longitudinal distribution of recoil electrons seems to have been made.

Jauncey's theory shows also that more recoil electrons would be ejected in the plane at right angles to the electric vector of a polarized X-ray beam than in the plane containing the electric vector. In other words, the lateral distribution of recoil electrons should show a maximum

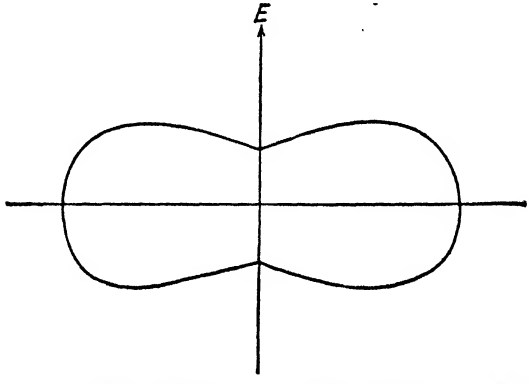


FIG. 11-19.—Lateral distribution of recoil electrons. (*Kirchner.*)

in a direction 90 deg from the electric vector—in striking contrast to the distribution obtained for the photoelectrons. This point has recently been tested experimentally by Kirchner,[4] who finds the distribution curve shown in Fig. 11-19. It is evident that there is a concentration of electrons in a direction 90 deg from the electric vector. This type of distribution is just what would be expected when it is recalled that a polarized beam of radiation is not scattered at all in the direction of the electric vector. Since the paths of the scattered quantum and of the recoil electron must lie in the same plane, the total number of recoil electrons ejected *in the plane of* the electric vector should be less than for a plane at right angles thereto. (It should be remembered that the lateral distribution curves for recoil electrons represent the distribution of the *components* of the electron velocity which lie in a plane perpendicular to the direction of the X-ray beam. Actually there are no electrons ejected *in* this plane.)

[1] H. COMPTON and J. C. HUBBARD, *Phys. Rev.*, **23**, 439 (1924).

[2] G. E. M. JAUNCEY, *Phys. Rev.*, **23**, 580 (1924).

[3] It is evident from Eqs. (11-23) and (11-25) that the energy of a recoil electron depends on its direction of ejection (in striking contrast to photoelectrons). The energy is a maximum for $\theta = 0$ and is zero for $\theta = 90$ deg. Hence recoil electrons ejected at large angles will not be observed in expansion-chamber experiments.

[4] F. KIRCHNER, *Phys. Zeits.*, **27**, 385 and 799 (1926); *Ann. d. Phys.*, **81**, 1113 (1926)

CHAPTER XII

PHOTOELECTRIC TECHNIQUE

This chapter is concerned with the design, preparation, and use of photoelectric cells, and with other topics associated with investigations in photoelectricity (*e.g.*, sources of light, monochromators, light filters, etc.). We are not concerned here with fundamental laws, nor with the application of photoelectric cells. Strictly speaking, every problem calls for its own special technique; nevertheless it is possible to review briefly the general methods which should be familiar to every student of the subject.

TYPES OF PHOTOELECTRIC CELLS

The following factors are important in designing a photoelectric cell and choosing the active metal: (1) the spectral region available, (2)

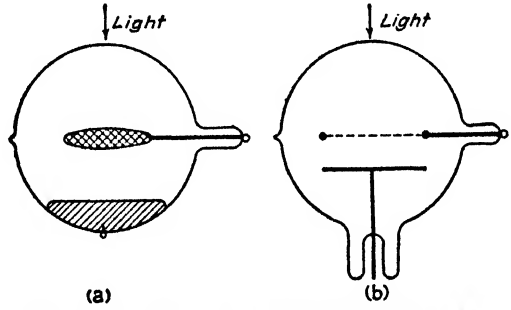


FIG. 12-1.—Simple types of photoelectric cells.

the intensity available, (3) whether large electric currents are required or not, (4) whether extreme constancy of behavior and linearity of response are required, (5) the width of the beam of light, and (6) the space available for the cell. The purposes for which cells are required may be divided broadly into two groups:

A. Applications calling for the production of an electric current which is a known and reproducible function (preferably linear) of the intensity of the light.

B. Relay or "trigger" applications in which all that is required is the production of a sufficient change in the electric current when the light intensity crosses a certain value.

The demands in case *B* are not so severe as in case *A*, but a large (current/intensity) ratio is always desirable.

12-1. Design of Cells.—The simplest types of cell have plane electrodes as in Fig. 12-1. Figure 12-1*a* represents a cell containing an alkali metal, which is run into position while molten. The anode may be a single wire, a grid, or a plate (with suitable provision to allow the light to get to the cathode). In other types of cells, one electrode almost completely surrounds the other (Figs. 12-2 and 12-3). The cathode in Fig. 12-2 consists of a layer of an alkali metal which has been condensed on the inside walls of the cell. A small patch is cleared away by the application of a small flame locally, leaving a *window* for the light to enter. This type of cell is sometimes referred to as a "black-body" type cell, because practically all the light which enters is captured and is usefully employed in producing photoelectrons.[1] This advantage over a plane type of cathode occurs only when the surface is highly reflecting, as in the case of pure alkali metals. When modern "sensitized" surfaces, which are well colored and therefore absorb the light strongly, are used, the advantage is much less, for most of the light is absorbed when the beam first strikes the surface.

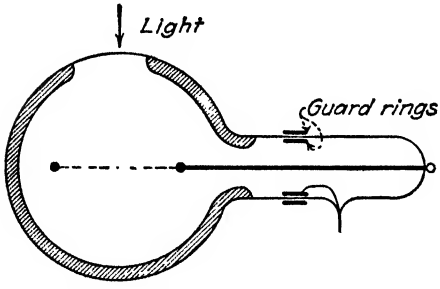


FIG. 12-2.—Spherical photoelectric cell.

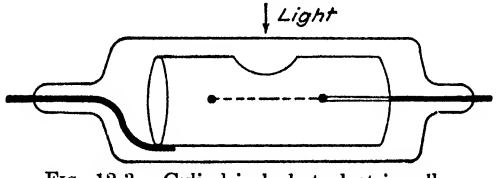


FIG. 12-3.—Cylindrical photoelectric cell.

When the cells are used to measure currents below about 10^{-12} amp, special precautions are necessary to secure the highest insulation. To effect this, inside and outside guard rings of metal are provided, as in Fig. 12-2, so that the glass between the central electrode (which is the one ordinarily connected to the electrometer) and the guard ring has to insulate against only a fraction of a volt instead of against the full voltage between the anode and cathode. The inside glass surface after a thorough outgassing is usually an excellent insulator, provided that an invisible film of alkali metal does not condense on it. The outside glass surface, unless it can be kept in a perfectly dry atmosphere, is apt to be a poor insulator, and so it is usually coated with some wax (sealing wax, Khotinsky cement, etc.) while warm. The foregoing precautions are

[1] A. L. HUGHES, *Phil. Mag.*, **25**, 679 (1913).

usually required when currents are such that an electrometer is necessary to detect them; with larger currents (*i.e.*, $> 10^{-10}$ amp), such as can be detected by a galvanometer, they are not so necessary. This is especially true when pyrex glass is used. Indeed, most commercial cells do not have guard rings; they rely wholly on the glass for insulation.

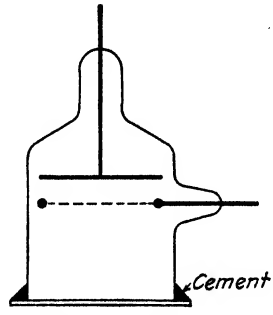


FIG. 12-4.—Cell with quartz window.

Frequently commercial cells do not show a linear relation between the photoelectric current and the intensity of the light. In many cases this has been traced down to the presence of insulating surfaces in the cell, so placed that photoelectrons can accumulate on them, thereby distorting the field and modifying the current. In other cases, when the metal layer on the inside of the glass cell is the cathode, the invisible alkali-metal film over the window contributes irregularly to the total current, because of its imperfect conductivity. The last trouble can be avoided by using the central electrode as cathode, or by mounting the cathode independently of the glass, as in Fig. 12-3. In any case, it is well to arrange to have as little exposed insulating surface as possible within the cell, and to arrange as far as possible to have it where neither light nor electrons can hit it. Further comments as to the departure from linearity in cells will be found in Sec. **2-8**.

Pyrex glass and other common glasses cease to transmit at about 3300A. Consequently, for use in the ultra-violet, cells should be made of fused quartz or should be

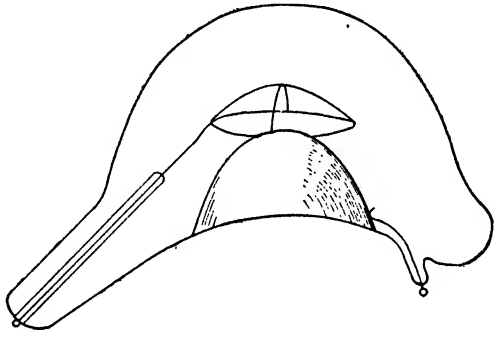


FIG. 12-5.—Kunz's cell.

provided with quartz windows. The quartz window may be attached to the cell by sealing wax or Khotinsky cement (Fig. 12-4). Should it be necessary to outgas the cell, then a "graded seal" between quartz and glass would have to be used.

A special type of cell for recording sunshine is shown in Fig. 12-5 (Kunz).[1] The peculiar shape is to allow the sunshine to fall at much the same angle on a sensitive surface, no matter where the sun is.

Voltage-current relationships for spherical cells have been investigated by Ives.[2] When the cathode is a small sphere mounted inside an enclos-

[1] J. KUNZ and V. E. SHELFORD, *Rev. Sci. Instr.*, **1**, 106 (1930).
[2] H. E. IVES, *Bell Syst. Tech. Jour.*, **5**, 320 (1926).

ing anode and both are in a vacuum, the photoelectric currents become saturated at or near zero volts (Fig. 12-6). This is because no photoelectrons leaving the central cathode can return to it when the field directs them away from it, no matter how small it is. (The same type of curve should be obtained for plane electrodes.) When, however, the cell consists of a spherical cathode surrounding a small anode, as in Fig. 12-2,[1] voltage-current curves of the kind shown in Fig. 12-7 are obtained. The lack of saturation is due to the fact that the photoelectrons start off initially in all directions with small but finite initial velocities. When there is but a small field accelerating them to the central anode, they are frequently not sufficiently deviated to be drawn into it, and so miss it and contribute nothing to the current. Hence a considerable accelerating field is necessary to pull all the photoelectrons into the central anode,

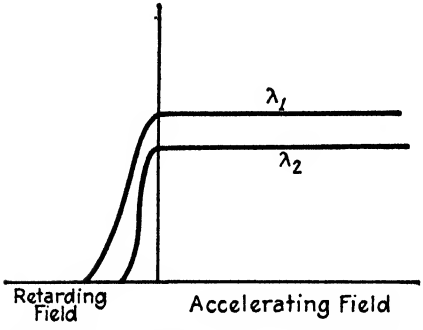


FIG. 12-6.—Voltage-current curves for central cathode cells ($\lambda_1 < \lambda_2$).

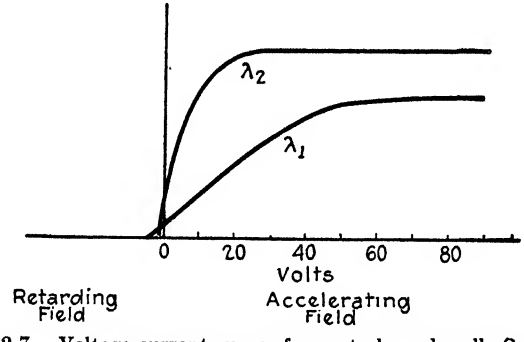


FIG. 12-7.—Voltage-current curves for central anode cells ($\lambda_1 < \lambda_2$).

and clearly this is *larger* the larger the initial random energies of the photoelectrons, *i.e.*, the *smaller* the wave-length of the exciting light. From a theoretical standpoint the problem is one of central orbits in which we have a large number of electrons starting off in random directions with given speeds, and for which we have to calculate the fraction of orbits intercepted by the central sphere for each accelerating field. This was carried through by Ives and Fry,[2] the results being in qualitative accordance with Fig. 12-7.

[1] The cell used by Ives differs from that shown in Fig. 12-2 in that he used a small sphere for the inner electrode.

[2] H. E. IVES and T. C. FRY, *Astrophys. Jour.*, **61**, 1 (1922). See Sec. 4-7.

12-2. Alkali-metal Cells.—The methods of using alkali metals in photoelectric cells may be classified as follows:

Thick Layers.[1]
1. Clean surfaces.
2. Surfaces sensitized by a glow discharge in hydrogen.
3. Surfaces sensitized by suitable exposure to certain gases and vapors.

Thin Films.
4. On clean supporting metals, *e.g.*, Pt, Ag, Cu, Mg.
5. The same and then sensitized by a glow discharge in hydrogen.
6. On a supporting metal whose surface has been altered by adsorption of, or perhaps chemical action with, certain substances, *e.g.*, O_2, S, Se, H_2O, . . .

1. To prepare cells with surfaces of the first type, the cell is thoroughly outgassed and the metal, previously distilled several times, is evaporated into the cell, where by suitable application of a flame it is distributed where required. As a rule the alkali metal is deposited on the inside of the tube, so forming a cell approaching the black-body type. The surface is silvery in appearance. The sensitivity and the threshold depend on the outgassing. Provided that the outgassing is not *extremely* thorough, such cells show considerable spectral selectivities, with maxima and thresholds roughly as follows:

TABLE 12-1.—PHOTOELECTRIC CHARACTERISTIC OF CLEAN ALKALI METALS

Metal	Li	Na	K	Rb	Cs
Maximum of spectral selectivity....	2800A to (4050A?)	3400A to (4200A?)	4200A to 4400A	4600A to 4800A	4800A to 5500A
Threshold.....	.. ..	5700A	5800A	6000A	6500A

This table is constructed in part from Table 5-2.

The relative emissions for different alkali-metal surfaces prepared in comparable ways have been determined by Seiler[2] (Fig. 12-8). Those given by Campbell and Ritchie[3] are in fair agreement, except that the probable maximum yield for Na is less than that found for K, a result contrary to Seiler's. However, there is no certainty that in Seiler's work, in which gas-filled cells were used, the ionization-by-collision factor was always the same.

2. Passing a glow discharge through hydrogen at a low pressure in contact with the surface produces brilliant surface colors and a con-

[1] As in Chap. V, a "thick layer" is one in which the photoelectric effect is characteristic of the metal in bulk. A layer, 100 atoms thick, probably satisfies this criterion. A "thin film," on the other hand, is seldom more than two or three atoms thick and its photoelectric properties are different from those of a thick layer of the same substance.

[2] E. F. SEILER, *Astrophys. Jour.*, **52**, 129 (1920).

[3] N. R. CAMPBELL and DOROTHY RITCHIE, "Photoelectric Cells," p. 29 (Sir Isaac Pitman & Sons, 1929).

siderable increase in sensitivity (of the order of five- to twenty-fold) with a shift towards the red, both of the maximum and the threshold. Until recently this was the only practical way of producing photoelectric cells of high sensitivity.

3. The method of preparing surfaces of the third type is so new that improvement in technique will doubtless develop rapidly. Olpin[1] exposed thick layers of potassium and sodium to sulphur (and many other) vapors and found a great increase in sensitivity. Further discussion is found in Sec. **5-11.** Exposing a sulphur-treated surface to a glow discharge in hydrogen, as Olpin sometimes did, is a combination of 2 and 3.

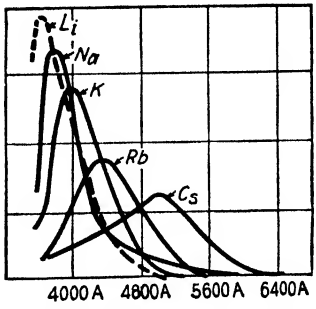


FIG. 12-8.—Relative sensitivity of alkali metals. (Author gave no information as to currents for Li relative to those for the other metals; curve given merely for position.)

4. These surfaces—due to Ives—have been considered in some detail in Sec. **5-4.** They are produced most easily by first depositing the alkali metal over the surfaces inside the cell. Then, by gentle heating (sufficient to produce rapid evaporation from the alkali metal in bulk), all the metal but a thin film, requiring much higher temperatures to dislodge it, is driven out of the cell, after which it may be sealed off. The characteristics, already discussed, include a threshold at a wave-length not greater than that of the first line of the principal series of that element, a considerably higher sensitivity than the metal usually shows when in thick layers, and no spectral selectivity at any wave-length $>$ 3800A.

5. Campbell showed that an enormous increase in sensitivity to white light, mainly due to a shift in the threshold to the red and infra-red, could be obtained by sensitizing the thin films, prepared as in 4, by a glow discharge in hydrogen.

6. We now have a bewildering variety of surfaces in the last class, chiefly due to Olpin's researches. In class 3 we mentioned the improvement in sensitivity resulting from the exposure of a thick layer of K or Na to a variety of vapors. If now a thin film of an alkali metal (by evaporation from a side tube) be deposited on top of this treated surface, a remarkable improvement in sensitivity, mainly due to a shift of the threshold into the red, is found. Previous to Olpin's work, Koller had produced very sensitive surfaces of thin films of Cs on CsO on Ag, possibly the most sensitive surfaces to white light yet obtained.[2]

[1] A. R. OLPIN, *Phys. Rev.*, **36**, 257 (1930).

[2] L. R. KOLLER, *Jour. Opt. Soc. Amer.*, **19**, 135 (1929). The nature of the oxide is unknown; "CsO" is merely a convenient label. Very recent experiments by E. F. Kingsbury and G. R. Stillwell (*Phys. Rev.*, **37**, 1549 [1931]) have shown that a high thermionic emission at room temperature seems to be a property of these Cs on CsO

It is convenient here to summarize the sensitivity of various alkali metals in terms of the photoelectric current obtained with white light. While this is not so precise a method of description as that in which we state the yield in coulombs per calorie at each wave-length, it is frequently used, because in most commercial applications the cells are illuminated by white light. The extraordinary sensitivity of the Cs-CsO-Ag surface is due to two factors: (1) the wide range, extending into the infra-red, over which the surface is photoelectrically active; and (2) the fact that the concentration of energy in the spectrum of a tungsten lamp is a maximum in the infra-red and is relatively very small in the blue and ultra-violet, where the plain alkali metals are most sensitive.

TABLE 12-2.—WHITE LIGHT YIELD OF PHOTOCELLS

Material		Yield, microamp/lumen	Authority
Thick layers of	Na	0.5	Campbell and Ritchie (Source: W at 2650°K)
	K	1.0	
	Rb	0.44	
	Cs	0.17	
Thin films of	K on CuO	0.8	
	Cs on CsO on Ag	15 to 40	Koller
	Na on S	7.0	Olpin (Source: W at 2848°K)

In view of the large variety of surfaces available, and in view of the difficulty of comparing data given by different investigators, it is far from easy to make dependable comparisons between the various results. But, inasmuch as definite recommendations may be desired by those who propose using photoelectric cells, we make the following specific suggestions as to the kind of surfaces to be used under different circumstances:

A. If a high yield is not a prime consideration, surfaces of pure K and Na (in thick layers) should be useful for light of wave-length shorter than about 5000A or 5500A. The Na is to be preferred if it be desired to accentuate the effect of the region 3500A to 4500A. One advantage

cells. Thus they find thermionic currents of the order of 10^{-9} amp at 20°C, with a temperature coefficient of the order of 10 per cent per 1°C. Consequently, when measuring photoelectric currents of this order of magnitude, it would be necessary to hold the temperature of the cell very constant. It would also appear to be impossible to take advantage of the remarkably high sensitivity of these cells to measure small light intensities by the small photoelectric currents (*e.g.*, 10^{-14} amp) produced, except by reducing the temperature of the cell very considerably. This remark has a bearing on Sec. 12-14.

of the clean untreated surface is that its photoelectric characteristics are permanent and reproducible.[1]

B. If the highest possible yield in the region 4000A to 5000A (and especially around 4400A) be desired, the best surface to use is a thick layer of K, sensitized by a glow discharge in hydrogen. Commercial photoelectric cells often contain such surfaces.

C. Should a high yield be desired in the region 4000A to 7000A (corresponding roughly to what the eye sees best), a surface consisting of a thin film of Cs on CsO on Ag is excellent. It should be added, however, that slight variations in the mode of making this surface have a considerable effect on the spectral distribution. Some of these cells have a maximum yield at about 7500A and have a threshold not far from 10,000A. Consequently they are excellent for the near infra-red. Instructions as to how these surfaces should be prepared will be found in Sec. **12-5.**

It should be emphasized that we do not recommend *A*, *B*, and *C* because of an established unquestionable superiority over all other surfaces now available; they were selected because they have been tried out by various investigators and found to be extremely satisfactory. Further research—finished perhaps before this book is published—may bring forth surfaces which are undoubtedly better than *A*, *B*, and *C* for their respective purposes.

Olpin[2] has very recently published interesting curves showing the spectral distribution of some of the new composite surfaces (Fig. 12-9). It is evident that a cell containing Na treated with S and O would make the best "artificial eye" if provided with a filter to match the visibility curve.[3]

12-3. Other Metals.—Metals outside the alkali-metal group have been used but little in photoelectric cells. The reason is obvious; there is comparatively little commercial need for devices responding only to ultra-violet light. However, for certain specific purposes, the restriction of response to the ultra-violet may be a definite advantage. Metals of the alkaline-earth group, Ca, Ba, and Sr, have characteristics analogous to those of the alkali metals, but displaced somewhat towards

[1] A cell with very permanent characteristics may be prepared by electrolysing Na through glass in the manner developed by R. C. Burt (*Phil. Mag.*, **49**, 1168 [1925]). See also L. Marton and E. Rostas, *Zeits. f. Tech. Phys.*, **10**, 52 (1929); *Zeits. f. Instr.*, **59**, 578 (1929).

[2] A. R. Olpin, *Bell Lab. Record*, **9**, 310 (1931).

[3] Since this section was written, the following papers on matters related to it have appeared: "The Wave-length Sensitivity Curve of a Caesium Oxide Photocell; a New Light Sensitive Instrument for the Ultra-violet" by T. F. Young and W. C. Pierce (*Jour. Opt. Soc. Amer.*, **21**, 497 [1931]); "Photoelectric Cells in Colorimetry" by H. E. Ives and E. F. Kingsbury (*Jour. Opt. Soc. Amer.*, **21**, 541 [1931]); "Photocells in Theory and Practice" by V. K. Zworykin, (*Jour. Franklin Inst.*, **212**, 1 [1931]).

the ultra-violet. Ba and Sr both show spectral selectivity with maxima at 2800A and 3400A and with thresholds at 5500A and 6000A, respectively. It is probable that the distinctions between these characteristics, and those of Li and Na, are not sufficiently pronounced to call for the development of a special technique in the construction of cells containing Ba, Sr, or Ca. No systematic study of methods of sensitizing these metals (*e.g.*, by a glow discharge in hydrogen) appears to be on record. However, Case[1] has made cells with thin films of Ba on a metallic plate, which are sensitive to the red.

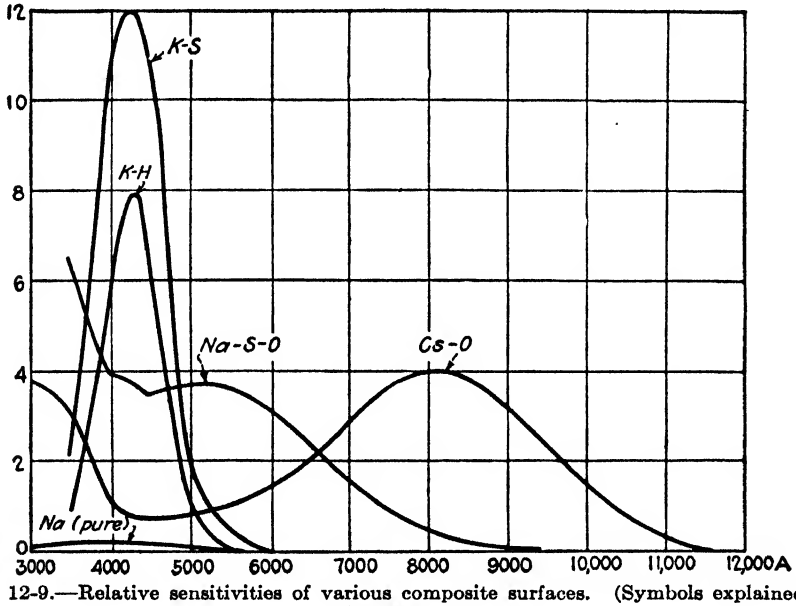


FIG. 12-9.—Relative sensitivities of various composite surfaces. (Symbols explained in Sec. 5-11.)

For studies requiring response to the near ultra-violet, but not to the visible, the metals Al, Zn, and Cd are probably the most useful. If it be desired to have surfaces which respond only to wave-lengths shorter than about 3000A, Fe, Ni, and Co should be suitable. The thresholds for a large number of metals cleaned by sandpapering in air just before putting into a cell, have been determined by Hamer.[2] As a cell, prepared in this way, is easier to construct than one involving distilled metals or outgassed metals, and is adequate for many applications, Hamer's thresholds may be useful in selecting the metal to use. It is conceivable that occasionally it might be desirable to secure a cell responding only

[1] T. W. CASE, "Photoelectric Cells and Their Applications; a Discussion at a joint meeting of the Physical and Optical Societies," p. 50. (Published by the Physical and Optical Societies, London, 1930.) Hereafter this publication will be referred to as "Discussion on Photoelectric Cells."

[2] R. HAMER, *Jour. Opt. Soc. Amer.*, **9**, 251 (1924); see Sec. 3-21.

to light of wave-length shorter than 2000A. For this purpose extremely well-outgassed platinum, or tungsten coated with oxide,[1] should be used.

As to the yield of these metals in the ultra-violet, unfortunately practically nothing which could be helpful in the selection of a suitable surface is on record. (de Lazlo, however, gives figures showing that the yield of magnesium rises to the value of 5.2×10^{-2} coul/cal at 2536A, a yield which is comparable to the very best yields of sensitized potassium at its own maximum.[2] No statement is made as to whether any special mode of preparation is needed to produce this result.) It is worth recording here that Thomas[3] increased the sensitivity of an Al cell (to 2536A) seventy-five fold by passing through it a glow discharge in hydrogen, without shifting the threshold far enough to make it sensitive to daylight.

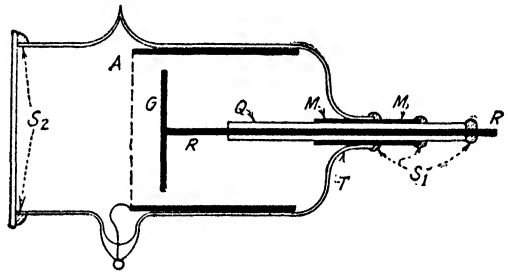


FIG. 12-10.—Photoelectric cell for the ultra-violet.

12-4. Methods of Introducing Metals into Photoelectric Cells.—While many excellent cells are now available commercially, some may desire to make their own, and there may be certain investigations for which the cells on the market are, for some reason or another, not wholly suitable. We therefore give an outline of the methods by which cells are made.

The simplest cells to make are those in which metals like Cu, Ni, or Zn, cleaned in air, are used as cathodes. Figure 12-10 shows how such cells may be assembled. G, the plate to be illuminated, is carried on a rod R which fits snugly inside a quartz tube Q. This in turn is separated from the glass tube T by a metal tube M, the fit everywhere being good. (M is the guard ring.) Sealing wax, picein, or Khotinsky cement, melted on to the glass, quartz, and metal, while these are hot, serves to make the joints at S_1 air-tight. The quartz window is fixed on in the same manner at S_2. To secure the highest insulation the quartz tube Q must be carefully cleaned with acids and distilled water and then dried, after which it is advisable to put it in place without fingering it. The anode, A,

[1] See Sec. 3-12 and 3-15.

[2] H. DE LAZLO, "Discussion on Photoelectric Cells," p. 221 (see footnote 1, p. 427).

[3] A. R. THOMAS, *Phys. Rev.*, **35**, 1253 (1930).

consists of a metal tube lining the glass tube and covered at one end with a grid. A tube so constructed may be used with an electrometer to measure currents down to 10^{-15} amp. If galvanometer currents (*i.e.*, $>$ 10^{-10} amp) are to be studied, the tube may be simplified by the omission of the guard ring, the quartz insulation, and the tubular part of the anode (whose purpose is electrostatic shielding). The surface of G should be cleaned thoroughly with sandpaper just before the cell is assembled. Since this cell cannot be outgassed, it should be left on the pump for several hours before being sealed off.

The wax seals in a cell of this kind render it useless for the study of photoelectric effects in gas-free metals, but for comparing intensities in the ultra-violet such a cell is valuable and has the merit of being easily made. If a cell which can be outgassed be desired, then one must use "graded seals" between quartz and glass to take the place of the joints made air-tight by cement.

The technique of making an alkali-metal cell is quite different, because the sensitive surface cannot be exposed to air. If we wish to make a spherical-type cell out of a 250-cc pyrex flask, we proceed as

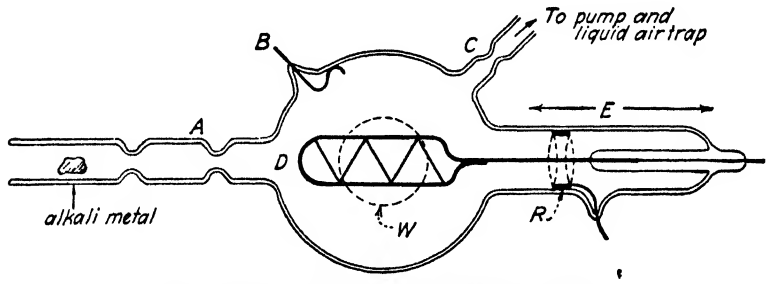


FIG. 12-11.—Alkali-metal photoelectric cell.

follows. Three side tubes, A, B, and C, are fused on to it (Fig. 12-11). After cleaning and drying, the inside is lined with a supporting metal. This may be either (*a*) silver deposited from any suitable silvering solution, (*b*) platinum deposited by burning off a "platinum paint" (*e.g.*, *Platinglanz*), or (*c*) tungsten or platinum deposited by evaporation from an incandescent filament (this process requires a good vacuum) or by cathodic sputtering. Proper precautions will insure that the lining makes good electrical contact with the wire sealed through B, and that it does not cover the part of the bulb finally to be the window. An internal guard ring R is most conveniently made by painting the inside of the tube locally with a ring of *Platinglanz* and burning it off to reduce the platinum. This is connected, through a seal, to the outside guard ring consisting of several turns of wire wrapped tightly round the outside. The anode D may be a rod, or an open lattice made by stringing fine wire

between two heavier wires as shown. If K or Na is to be used, then a small piece, freshly cut, is put into the end of A, which is immediately sealed up.[1] (On account of the cost of Rb and Cs, it is best to prepare these metals in the vacuum. A mixture of Ca filings and CsCl (or RbCl) is placed in A. After the vacuum has been obtained, the alkali metal may be produced by heating the mixture.) A vacuum is produced in the cell as soon as possible, and the cell is well outgassed by heating all except the part of A containing the alkali metal. After the cell has cooled the alkali metal is slowly distilled from one bulb of A to the next, until it is finally distilled into the cell itself. By keeping E hot, the metal may be kept from depositing here. Finally after A and C are sealed off, a window may be produced at W by the cautious application of a small flame. To secure high insulation externally, the end of E, through which the anode passes, is covered with sealing wax while it is still hot. If the cell is to give "galvanometer currents" (*i.e.*, $> 10^{-10}$ amp), the guard rings and sealing wax may be omitted. The same procedure may be followed with obvious modifications in making a cell in which the cathode is separated from the walls as in Fig. 12-3.

To make photoelectric cells with Li as the sensitive surface, a special technique has been developed by Ives.[2]

If one requires photoelectric cells with a high yield, it is well to remember that, while outgassing no doubt makes for constant characteristics in a cell, extreme outgassing, lasting over many hours, leads to a very small yield (Sec. **5-10**).

12-5. "Thin Film" Cells.—To make a cell in which the sensitive surface is a thin film, the procedure in the previous section may be followed to just beyond the point at which the alkali metal is introduced into the cell. The whole cell is now gently warmed until all the alkali metal, so far as the eye can tell, is driven out of it. A monatomic layer of alkali metal will be left on all the metallic supporting surfaces, which cannot be dislodged so long as the temperature is kept well below 300°C.[3] The cell may now be sealed off. (Should a cell of the type shown in Fig.

[1] It is more convenient perhaps to outgas a large quantity (*e.g.*, 20 cc), of the metal in an auxiliary apparatus, and to run off the clean metal into glass tubes (about 5 mm diameter and 20 mm long) which are then sealed off. When a cell is to be made, one of these tubes, with its tip broken off, may be placed in A, instead of a lump of metal.

[2] H. E. Ives, *Phys. Rev.*, **34**, 117 (1929); also E. F. Seiler, *Astrophys. Jour.*, **52**, 549 (1920).

[3] It may be inferred from the work of Ives that much stronger heating is required to drive off a monatomic layer of alkali-metal atoms from a supporting metal than to drive off the same atoms from a thick layer of the alkali metal itself. This characteristic may make it possible to secure better insulation in thin-film photoelectric cells than in cells containing a considerable amount of the metal where the insulating glass surfaces tend to become covered with a slightly conducting invisible film.

12-3 be needed, it would be necessary to warm the isolated cathode cautiously by an induction furnace, since the vacuum is a very good heat insulator.)

Zworykin and Wilson[1] have found that a magnesium lining in a photoelectric cell forms an excellent supporting material for Cs. (It is possible, however, that here we are dealing with something more like a compound between Cs and Mg than with a monatomic layer of Cs on Mg.)

12-6. Sensitization by a Glow Discharge in Hydrogen.—If it be desired to increase the sensitivity by means of a glow discharge in hydrogen, provision must be made for introducing hydrogen at a low pressure into the cell. The most convenient way to effect this is to have a palladium tube, closed at one end, fused into a glass tube which is part of the pumping system.[2] The hydrogen is introduced by merely making the tip of the palladium tube red hot for a few seconds with a gas flame. A glow discharge is passed through the cell by means of a small induction coil, a step-up transformer, or a 1000-volt direct-current generator. The surface of the metal becomes brilliantly colored and the photoelectric yield may increase by a factor of 40. (This is necessarily vague, for it depends considerably on the kind of light used to study the increase in the yield. The factor 40 is given by Nottingham,[3] who used white light.) The length of time for which the glow discharge should pass, the strength of the discharge, whether it should be alternating or direct, and, in the latter case, whether the alkali-metal surface should be cathode or anode, all seem at the present time to be largely matters of taste. Thus Nottingham[3] flashes a discharge for an instant, then tests for sensitivity, flashes a discharge for an instant, then tests for sensitivity, flashes a discharge again, and so on, until a maximum sensitivity is attained, which means a total discharge period of but 2 or 3 sec. Campbell and Ritchie,[4] on the other hand, imply that it is better to continue the discharge for several hours.

A detailed account of a method of making a sensitized photoelectric cell is given by Nottingham.[3]

12-7. Sensitization by Other Methods.—We shall here outline the method of producing a surface of Cs on CsO on Ag as the supporting

[1] V. Zworykin and E. D. Wilson, *Jour. Opt. Soc. Amer.*, **19**, 81 (1929).

[2] It is a matter of some difficulty to seal a palladium tube into glass. We have found it convenient to seal a closed palladium tube (1 mm internal diameter) into a soft glass tube, so that about 6 cm of the palladium tube projects, and to cover the seal where the glass is liable to crack with sealing wax. This may be kept cool by wet cotton while hydrogen is being admitted.

[3] W. B. Nottingham, *Jour. Franklin Inst.*, **206**, 637 (1928).

[4] N. R. Campbell and Dorothy Ritchie, "Photoelectric Cells," p. 96 (Sir Isaac Pitman & Son, 1929).

metal.[1] Such a surface, when properly prepared, is extremely sensitive to the red and near infra-red. The supporting layer of Ag is obtained either by evaporating the metal on to the walls of the cell, or merely by making the cathode out of silver sheet. After the usual preliminary outgassing, oxygen is admitted to the cell and an electric discharge passed through it until a layer of Ag at least 10 molecules thick is oxidized. (This is denoted by a characteristic blue color.) With the cell maintained at about 200°C, Cs vapor is admitted from a side tube and reacts with the oxidized silver. The thermionic emission from the surface is measured while the Cs is entering. As the reaction proceeds, the thermionic emission increases to a maximum and then falls very suddenly. This indicates that the surface has passed its most sensitive state. The admission of Cs vapor must now be stopped and the excess Cs must be driven off the surface by continuing the heating for about half an hour. The cell may then be sealed off the pump. The preparation of cells of high sensitivity appears to be more of an art than a science at the present time.

Olpin[2] has discovered a variety of ways of sensitizing various alkali metals by suitable exposure to one or other of a large assortment of vapors, dyes, and organic substances. The original paper should be consulted.

12-8. Gas-filled Cells.—In all the cells previously described the last step in the operation just before sealing off was to secure a high vacuum. Cells so prepared are called vacuum cells. The presence of a gas in the cell enables one to use the ionization by collision effect to magnify the original photoelectric current many times. The only suitable gases to use are the inert gases, and of these the most suitable is argon, because the increase in current due to ionization by collision is greater with this gas than with helium or neon. This is due to the fact that argon has the lowest ionization potential. The inert gas may be purified by exposure for several hours to (1) an arc or discharge between Ca rods, or (2) an electron discharge between an incandescent filament and a pool of liquid sodium or potassium. The essential thing is to have copious ionization in the presence of a metal of high reactivity. A convenient way of determining the amount of inert gas to be introduced is as follows: The photoelectric cell, while on the pumping system, is connected to a galvanometer, a 100- or 150-volt battery, and a protecting resistance of over 10,000 ohms. It is now illuminated by a suitable steady source and the increase in current is carefully watched as the purified gas is slowly admitted. When the current attains its highest value—which usually will happen with pressures of the order of 0.2 mm—the cell should be sealed off.

[1] N. R. Campbell, "Discussion on Photoelectric Cells," p. 15 (see footnote 1, p. 427); we are indebted to Dr. Campbell for supplying us with additional information.

[2] A. R. Olpin, *Phys. Rev.*, **36**, 251 (1930); see also Sec. 5-11.

Koller[1] recommends that the gas pressure should be somewhat less than that giving the greatest ionization by collision in order to obtain greater stability. He also states that these gas-filled cells will retain their characteristics unchanged when the applied potential is below 100 volts, whereas when it exceeds 120 volts the emission falls off in the course of a few hundred hours.

Gas-filled cells are generally used under conditions of pressure and applied voltage such as to give magnifications of the original photoelectric current of the order of ten times. Much larger magnifications can be obtained by cautiously increasing the applied potential up to a value just short of that necessary to start a self-maintained discharge.[2] Campbell and Ritchie[3] state that marked departure from proportionality between light intensity and current begins in gas-filled cells when the current exceeds 2 or 3 microamp.

Further information as to the preparation of photoelectric cells may be found in the articles cited in the footnote.[4] An apparent lack of proportionality between the current in a gas-filled cell and the light intensity may sometimes occur when a protecting resistance is used in series with it (see Sec. **12-15**). Attention should be called to an inertia effect in gas-filled cells when they are used to follow fluctuations in light intensity of more than about 1000 cycles/sec (see Sec. **13-8**).

12-9. Vacuum Technique.—There are many experimental investigations in which it is desired to study or to make use of the photoelectric properties of perfectly *clean* metal surfaces. In such cases, granted that a chemically pure metal is introduced into the cell, the problems of prime importance are to free the metal surface of occluded gas layers and to maintain within the cell an extremely high vacuum. As we have seen in Chapter III, the photoelectric and thermionic properties of surfaces may be profoundly affected by the slightest traces of residual gas, the removal of which is usually a difficult task. Probably no one has been able to work with *really* gas-free surfaces, but it has been found possible, using modern high-vacuum technique, to eliminate the erratic behavior characteristic of surfaces containing traces of gas. The methods which have been employed for accomplishing this have already been discussed in Chapter III, and the general methods of high-vacuum technique have been adequately reviewed in treatises on the subject.[5]

[1] L. R. Koller, *Jour. Opt. Soc. Amer.*, **19**, 135 (1929).

[2] J. Elster and H. Geitel, *Phys. Zeits.*, **17**, 268 (1916).

[3] N. R. Campbell and Dorothy Ritchie, "Photoelectric Cells," Chaps. V–VII (Sir Isaac Pitman & Sons, 1929).

[4] N. R. Campbell and Dorothy Ritchie, *loc. cit.*, L. R. Koller, *loc. cit.;* H. E. Ives, *Bell Syst. Tech. Jour.*, **5**, 320 (1926); W. B. Nottingham, *Jour. Franklin Inst.*, **205**, 637 (1928); J. Kunz and J. Stebbins, *Phys. Rev.*, **7**, 62 (1916).

[5] S. Dushman, "High Vacuum," (General Electric Review, 1922); A. Goetz, "Physik und Technik des Hochvakuums" (Vieweg, 1926).

It may be well, however, to summarize briefly the precautions necessary to obtain "photoelectrically clean" metal surfaces.

1. It is assumed, of course, that an air-tight cell has been attached to an efficient mercury diffusion pump and that a liquid air trap is used to prevent mercury and other vapors from diffusing into the cell.

2. It is necessary that there be no sources of gas or vapor *within* the system. This means that there should be no waxed or greased glass joints on the high-vacuum side of the pumps, and that all glass and metal parts must be freed of residual gas. All waxes and greases have appreciable vapor pressures, and, even though these be as low as 10^{-6} mm Hg, they may greatly affect the photoelectric properties of metal surfaces. Furthermore, it is only by eliminating such joints that it is possible to heat all parts of the cell and connections to temperatures sufficiently high to drive off most of the occluded gases. For this purpose the glass parts are normally baked for many hours at the highest possible temperature (*e.g.*, 550°C for Pyrex) and the metal parts are heated at incandescent temperatures (by electron bombardment or high-frequency induction) until measurable evolution of gas has ceased. The importance of driving off residual gas may be realized when it is pointed out that a monomolecular layer of gas on a surface 10 cm^2 in area will, on evaporation into a cell whose volume is 200 cm^3, cause an increase in pressure of about 0.01 mm Hg. For photoelectric purposes it is often necessary to maintain a pressure of 10^{-8} mm Hg.

3. There remains the task of freeing the photoelectric surface itself of all traces of gas, as this surface must be far more thoroughly cleaned than other parts of the cell. In the case of alkali metals, clean surfaces are obtained by repeated distillation of the metal in vacuum before introduction into the exhausted cell. In the case of sodium good results have been obtained by electrolysis directly through the glass walls of the cell.[1] Freshly exposed surfaces of clean mercury have been produced by maintaining a continuous flow of the vacuum-distilled liquid.[2] In the case of the metals of higher melting point, however, cleaning of the surface can only be accomplished by prolonged heat treatment. The specimen is therefore usually prepared in the form of a wire or strip which can be easily heated by an electric current. The time required for the degassing process varies greatly with the metal and with the temperature at which it is heated. Tungsten may be thoroughly cleaned in a relatively short time (1 hr) at 2700°C, or in a few hours (*e.g.*, 10) at 2500°. It is probably impossible to remove all oxides by heating below 2000°C. On the other hand, platinum cannot be safely heated for long periods at temperatures higher than about 1400°C, and the time required for

[1] R. C. Burt, *Phil. Mag.*, **49**, 1168 (1925).
[2] C. B. Kazda, *Phys. Rev.*, **26**, 643 (1925).

degassing may be longer than 150 hr.[1] In recent experiments[2] with rhodium it was necessary to heat for over 1000 hr at 1200°C. The criterion for a clean surface is that its photoelectric or thermionic properties show no further change with heating at even the highest temperatures. If an ionization gage be used to measure the pressure, it should show no increase in pressure when the specimen is heated.

It has been found that after thorough degassing, combined with efficient pumping, the pressure in the photoelectric tube may be reduced to 10^{-8} mm Hg. At this pressure, gases will redeposit on the surface only very slowly,[3] and consistent measurements may be made. At higher pressures the rate of accumulation of gas becomes appreciable and the photoelectric threshold of the surface may change rapidly with the time after the heat treatment is stopped.

Some observers[1, 4] have found that the most satisfactory results are obtained, particularly when thermionic as well as photoelectric measurements are to be made, if, after long degassing, the cell is sealed off from the pumps and further traces of gas in the tube cleaned up by the use of a "getter." This method is now in common use, particularly in the industrial laboratories. The most satisfactory getters are magnesium, calcium, barium, and alloys of the rare-earth metals. Dushman and his co-workers[5] have recently found that "barium cleans up practically all residual gases at ordinary temperatures, while magnesium is ineffective in the case of hydrogen, and calcium does not take up nitrogen to any great extent." Extremely low pressures may also be maintained in a sealed-off cell by the use of well-degassed charcoal in a side tube immersed in liquid air.

MEASUREMENT OF PHOTOELECTRIC CURRENTS

Investigations involving the measurement of photoelectric currents range from those in which the photoelectric effect itself is the center of interest to those in which a photoelectric cell is merely a tool for indicating light intensities. The currents vary in magnitude from 10^{-15} amp to 10^{-3} amp; they may be constant or may fluctuate rapidly, and the required precision of measurement may vary considerably. Hence a wide variety of methods of measurement has been developed. The physicist, interested in the photoelectric effect itself, as a rule has to deal with currents between 10^{-11} amp and 10^{-15} amp; it is to be noted that he generally turns to an electrometer as the most convenient instru-

[1] L. A. DuBridge, *Phys. Rev.*, **29**, 451 (1927).

[2] E. H. Dixon, *Phys. Rev.*, **37**, 60 (1931).

[3] At a constant pressure of 10^{-8} mm it would require several hours for a monomolecular gas layer to form on a clean surface, assuming that *all* impinging molecules are adsorbed.

[4] A. H. Warner, *Proc. Nat. Acad. Sci.*, **13**, 56 (1927).

[5] S. Dushman, *Rev. Mod. Phys.*, **2**, 385 (1930).

ment to use. Those who use photoelectric cells merely as tools, especially for commercial purposes, often look askance at electrometers and prefer to use galvanometers. This is possible when the currents exceed 10^{-10} amp. Amplification of photoelectric currents by radio-tube circuits is now a common practice.

12-10. Electrometers.—The electrometers which are suitable for measuring photoelectric currents may be classified as follows:

1. Quadrant electrometer (best representative—Compton electrometer).
2. Lindemann electrometer.
3. Hoffmann electrometer.
4. String, fiber, and goldleaf electrometers.

1. The improvements in the Compton electrometer over its predecessors are due to a drastic reduction in dimensions, together with the introduction of a number of new adjustments.[1] A sensitivity of 5000 divisions/volt is easily attainable, and one of 50,000 divisions/volt is possible. The period, or rather the time required to complete a deflection (for it is aperiodic), is about 10 sec at a sensitivity of 5000 div./volt. It is very sensitive to changes of level and therefore has to be mounted on a steady platform.

2. The Lindemann electrometer is, in principle, a quadrant electrometer, but so changed in dimensions, shape, and disposition of the vital constituents as to be hardly recognizable.[2] A sensitivity of 500 div./volt is easily attained, and its period is about 1 sec. It is very robust (for it is mailed ready for use). Its great advantage is that it is quite insensitive to changes of level—in fact, it was originally designed to be mounted on a moving telescope.

3. The Hoffmann electrometer is the most sensitive instrument available.[3] According to Goetz, currents down to 10^{-18} amp can be detected by it but to attain this sensitivity extreme precautions and great skill are necessary. Once the instrument is adjusted, however, it is stable and easy to operate.

4. There are many varieties in this class. The principal feature, however, is a very light conductor (a goldleaf, or a platinized quartz fiber) hanging vertically between two plates charged to potentials of opposite sign. The conductor is in equilibrium between gravity and electrostatic forces. As the electric forces are increased the equilibrium becomes unstable. Just before this state is reached the slightest change in the potential of the hanging conductor is revealed by a deflection. A sensitivity of about 100 div./volt can be attained, with a period of

[1] A. H. and K. T. Compton, *Phys. Rev.*, **14**, 85 (1919).

[2] F. A. and A. F. Lindemann and T. C. Keely, *Phil. Mag.*, **47**, 577 (1924).

[3] A. Goetz, *Phys. Rev.*, **33**, 373 (1929); G. Hoffmann and W. S. Pforte, *Phys. Zeits.*, **31**, 822 (1930); W. Eggers, *Ann. d. Phys.*, **7**, 833 (1930); K. Engel and W. S. Pforte, *Phys. Zeits.*, **32**, 81 (1931).

about 1 sec. It is sensitive to changes of level. In the "string" type of electrometer (where the platinized fiber is attached below as well as above) the period is very short, and therefore the instrument is suitable for recording quick changes.[1]

12-11. Sensitivity of Electrometers.—The voltage sensitivity of an electrometer being given, the current sensitivity can be obtained if the capacity of the system (including electrometer, leads, and photoelectric cell) be known. We shall set up, as an arbitrary criterion of the smallest current detectable, that corresponding to a motion of one scale division in 60 sec. We have $i = Q/t = CV/t$, where i is the average current corresponding to the flow of Q coul in t sec, and C and V refer to the capacity and to the voltage change corresponding to the motion of the indicator (*e.g.*, the spot of light on the electrometer scale). Thus if $C = 200$ e.s.u. $= 200/(9 \times 10^{11})$ farads, and $V = 1/5000$ volt (corresponding to 5000 div./volt) and $t = 60$ sec, the current $i \sim 10^{-15}$ amp. The following table gives approximate data for the various electrometers under consideration.

TABLE 12-3.—TYPICAL ELECTROMETER CHARACTERISTICS

Electrometer	Period, seconds	Easily attained voltage sensitivity, divisions per volt	Capacity of an average set-up, e.s.u.	Order of minimum current detectable, ampere
Compton	10	5000	100	0.5×10^{-15}
Lindemann	1	500	20	1×10^{-15}
Hoffmann				1×10^{-18}
Fiber	1	100	20	4×10^{-15}

The characteristics of the Hoffmann electrometer are more readily expressed directly in current units.

The choice of the electrometer to be used in any investigation depends largely upon the special conditions prevailing. For a permanent set-up in which high sensitivity is required it is worth while mastering the use of a Compton electrometer. Should a portable outfit be required, then a Lindemann electrometer should be selected. Finally, for (photographically) recording rapid changes in a photoelectric current, the short period of a string electrometer is advantageous. The Hoffmann electrometer is coming into more common use in certain laboratories where extremely small currents are to be measured.

[1] All these electrometers, except the Hoffmann, are made by the Cambridge Instrument Company (Grand Central Terminal, New York, and Cambridge, England). Its catalogue contains practical information of a very useful kind.

12-12. Insulation and Shielding.—Insulation which is satisfactory enough when galvanometer currents (*i.e.*, $> 10^{-10}$ amp) are being measured, may be totally inadequate when much smaller currents, calling for electrometer methods, are to be registered. Only a few substances provide the necessary degree of insulation, *viz.*, amber, sulphur, and selected specimens of fused quartz. Hard rubber and sealing wax are nearly as good. In a photoelectric cell-electrometer system the most difficult place to secure first-class insulation is where the conductor enters the photoelectric cell. None of the insulators mentioned can be used here—except fused quartz—when it is necessary to avoid contaminating the vacuum by vapors. Wires cannot be sealed through fused quartz, and consequently, if fused quartz is to be used, there must be a graded seal between the fused quartz and the glass through which the metal wire is sealed. Cells have been made of fused quartz, with graded seals to glass wherever a wire is introduced. Such cells are bulky and expensive. It is possible to secure a high degree of insulation with certain kinds of glass (*e.g.*, Pyrex) provided care be taken. Defective insulation is nearly always a surface phenomenon. We have therefore to consider possible leakage over the inner and outer surfaces of the glass of the cell. With regard to the inner surface, the outgassing process which is an incident in the manufacture of the cell insures high insulation over the inner surfaces. If the cell contains an alkali metal, there still remains the possibility of a feeble conductivity over an invisible film of metal which may condense on the clear glass. This is less likely to occur with the newer thin-film cells, where the alkali metal is almost anchored down in place by a semichemical bond and the surplus driven away before the cell is sealed off, than with the older cells containing thick layers of the metal. With regard to the outer glass surface, the insulation may be kept high if the surface is never exposed to anything but absolutely dry air. When the current is small enough to call for electrometer methods of measurement, it is highly desirable to ground the guard rings (*M* in Fig. 12-10, *R* in Fig. 12-11), so that the glass has to insulate for only a fraction of a volt. Good insulation of the outer surface of the glass, even in the absence of very dry air, may be secured by coating with sealing wax, as mentioned in Sec. **12-1** and **12-4**.

When the photoelectric cell is connected to an electrometer, it is necessary to shield carefully the cell and the connecting wire by means of grounded metallic cases or tubes to prevent disturbances arising from electrostatic induction (Fig. 12-12).

These considerations with regard to high insulation and to shielding apply only to the case when the photoelectric cells are giving extremely small currents. If the currents are large enough to affect a galvanometer, such precautions are superfluous. In a photoelectric cell without a guard

ring the effect of imperfect insulation may be considerably diminished if the cell and galvanometer (or other indicating instrument) be connected to an *alternating* potential. The leakage current, since it reverses with

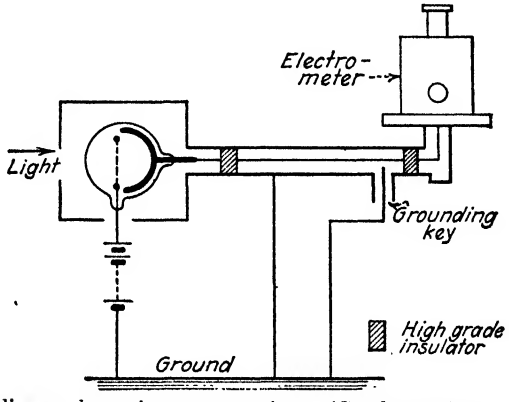


FIG. 12-12.—Shielding—schematic representation. (Conductor from cell to electrometer surrounded by grounded metal tube.)

the voltage, will not be registered, while the cell itself is a rectifier for the photoelectric current.[1]

12-13. Use of Electrometer. Null Methods.—The simplest method of measuring a current by an electrometer is to disconnect the grounding key (Fig. 12-12) and to determine the rate at which the indicator (the image of a filament on a scale, or the image seen through a microscope) moves across the scale. The current is proportional to the rate of motion, provided that this is slow enough to make the inertia effects of the moving system inappreciable. For most purposes only relative values of the current are required. Should absolute values be needed, one should know the capacity of the system, C, and the voltage sensitivity (to give the value of the change of potential, V, corresponding to the motion between the two marks of the scale between which the indicator moves in t sec). The current is then given by $i = Q/t = CV/t$. This method of measuring current should be used for currents which are too small to be measured by the modifications to be described presently. It has the disadvantage, however, that the scale, especially at high sensitivities, may be far from uniform, and that consequently calibra-

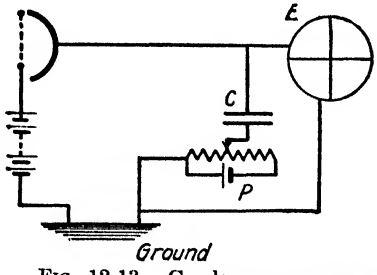


FIG. 12-13.—Condenser-compensation method. C. Small air condenser. P. Potential. E. Electrometer.

[1] P. SELÉNYI, "Discussion on Photoelectric Cells," p. 37 (see footnote 1, p. 427).

tion, or something equivalent to it, must be resorted to. The following modifications, in general, make for greater accuracy and convenience.

a. Condenser-compensation Method.—The previous arrangement (Fig. 12-12) is modified by the addition of a small air condenser as shown in Fig. 12-13. (From now on, the shielding in the diagrams is omitted for simplicity.) As the photoelectrons leave the illuminated surface in the cell, the potential of the insulated electrode-connecting wire-electrometer increases. This is compensated for by applying a suitable potential to the lower plate of the condenser C by means of the potentiometer. After a time t, the light is cut off and the potential applied to C is adjusted exactly until the electrometer deflection is zero. The average current is given by $i = CV/t$, where C is now the capacity of the small

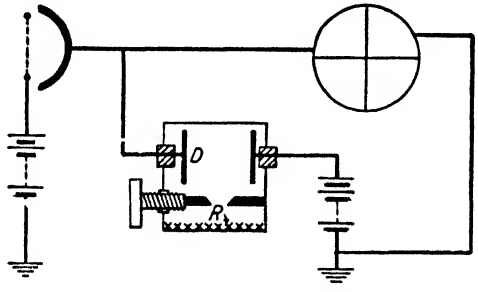


FIG. 12-14.—Ionization-compensation method. (Voltage on ionization chamber D sufficient to give saturation.)

condenser, and V the voltage supplied by the potentiometer. Besides being a null method, it has the advantage that the capacity C may be calculated from the geometrical dimensions of the condenser. A very compact assembly, including a Lindemann electrometer together with all the accessories for the condenser-compensation method, has been made by the Cambridge Instrument Company to the design of Moss.[1] It can be used in any position and is therefore particularly suitable for use with a photoelectric cell on an equatorial telescope.

b. Compensation by a Variable Ionization Current.—Here the photoelectric current is balanced by an ionization current produced in a chamber D by radiation from a uniform deposit of radioactive substance R (Fig. 12-14). (The active deposit from old radium emanation tubes used in the treatment of cancer is excellent.) Between the ionization chamber proper and the radioactive deposit there is a micrometer slit. After the initial calibration to check whether the amount of ionization is strictly proportional to the opening of the slit, the measurements of the photoelectric currents are carried out by reading off the aperture of the slit

[1] E. B. Moss, "Discussion on Photoelectric Cells," p. 76 (see footnote 1, p. 427).

opening when the ionization current just compensates the photoelectric current.

c. Resistance-shunt Method.—In this arrangement, the cell and electrometer are shunted to the ground by a high resistance R as in Fig. 12-15 (the potentiometer should be forgotten temporarily). A steady photoelectric current will now be shown by a *steady* deflection of the electrometer, and its value will be given by $i = V/R$, where V, the potential difference across R, corresponds to the electrometer deflection. This arrangement has the obvious advantage of making the electrometer indicate currents just like a galvanometer—a great advantage when it is necessary to secure a permanent photographic record of the current.

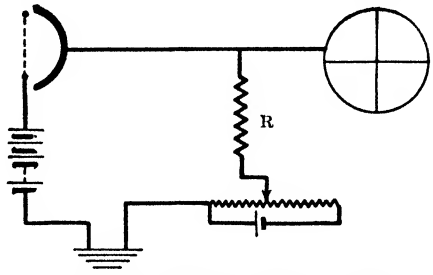


FIG. 12-15.—Resistance-shunt method.

To secure the advantages of a null method, all that is necessary is to apply by means of the potentiometer an opposing potential (which happens to be $-V$) to the lower end of R, until the electrometer deflection is zero. (This method can be used only for visual readings; it is, of course, inapplicable when recording is required.)

In principle, the sensitivity could be increased indefinitely by increasing R. Thus if $R = 10^{12}$ ohms, and if the voltage sensitivity be such that 1 division on the scale corresponds to $V = 0.0001$ volt, we could detect a current of 10^{-16} amp. The limit, however, is determined by the *time* taken to attain equilibrium. The equation $V = V_0 \exp (t/RC)$ tells us that the potential V_0 of the illuminated electrode and electrometer (while the light is on) drops to V in a time t after the light is cut off. We want this to be small enough so as not to slow down the taking of observations. As an arbitrary criterion let us consider equilibrium to be reached when $V = 0.01\, V_0$. Hence, with $R = 10^{10}$ ohms and $C = 90$ e.s.u. (10^{-10} farad), t turns out to be 4.6 sec. Since this is less than the period of a Compton electrometer, there would, with this instrument, be no appreciable decrease in the speed of taking observations. But if one used a Lindemann electrometer (period $\sim$ 1 sec) the speed of attaining equilibrium would be seriously impaired. It is evident that to get a high sensitivity by the resistance-shunt method we should use large resistances (10^9 ohms to 10^{11} ohms), but this calls for small capacities to avoid making the rate of attaining equilibrium unduly slow.

d. Resistances.—The resistances suitable for use in the resistance-shunt method just described should have values of the order of 10^7 ohms to 10^{12} ohms. ("Grid leaks" with resistances up to 10^8 ohms are made commercially.) Wire resistances are out of the question. The following materials have been used for such resistances.

α. Certain liquids[1] (*e.g.*, xylol alcohol mixtures).

β. Metallic films[2] (*e.g.*, Pt) sputtered or evaporated on to quartz or glass rods.

γ. India Ink lines[3] on paper.

δ. Lead-pencil lines.[4]

ϵ. Conducting glasses.[5]

ζ. Bronson resistances, and photoelectric cells operating far below saturation.

Among the requirements to be fulfilled by an ideal high resistance are (1) absence of polarization, (2) no departure from Ohm's law, (3) small temperature coefficient, (4) permanence. In our experience α, γ, and ϵ are easy to construct, but we have seldom found them to be totally free from polarization. A residual and variable polarization of the order of 0.005 volt frequently exists, just enough to interfere with accuracy of measurement. The sputtered metallic films β are totally free from polarization, obey Ohm's law, and have a small temperature coefficient. Their one defect is that they are troublesome to prepare and seldom retain a constant resistance over a period of many weeks. However, by following the technique developed by Van Atta,[6] a batch of resistors may be prepared of which perhaps a third or more may settle down to a constant resistance after a few weeks. We have not tested δ, but from the account published by Brewer it appears as though these resistors may be very satisfactory. An ionization chamber (in which the ionization is produced by a constant radioactive source) or a photoelectric cell may act as a satisfactory resistance ζ if the voltage-current relation for small voltages happens to be linear and to pass through the origin (*i.e.*, to obey Ohm's law). Such is the case approximately for small voltages. It is possible that a contact potential difference within the device would cause it to behave as though it had polarization; but we have had no experience with such devices. The effective resistance may be altered by changing the degree of ionization or the amount of light. The voltage-current relation sought is best fulfilled by a spherical-type photoelectric cell with a very small anode at the center. The resistance of any of these resistors may be determined by measuring the rate at which they discharge a condenser of known capacity. Two high resistances (provided the ratio of their values does not exceed 10:1) may be easily compared by a Wheatstone bridge if the usual galvanometer be replaced by a sensitive electrometer.

12-14. Measurement of Very Small Photoelectric Currents.—We shall now mention a selection of researches involving the measurement of extremely small photoelectric currents. They may be helpful to those planning investigations which call for the measurement of very small

[1] N. R. Campbell, *Phil. Mag.*, **23**, 68 (1912). For an alternative discussion of various types of high resistances, the reader is referred to N. R. Campbell and Dorothy Ritchie, "Photoelectric Cells," pp. 126–128 (Sir Isaac Pitman & Sons, 1929).

[2] L. C. Van Atta, *Rev. Sci. Instr.*, **1**, 687 (1930).

[3] The usual method is to draw a fine line with Higgins' Waterproof India Ink between two heavily inked areas on a strip of good paper. Pieces of tinfoil pressed into the inked areas serve as electrodes. The paper is then suitably mounted in a glass or metal tube for protection.

[4] A. K. Brewer, *Rev. Sci. Instr.*, **1**, 325 (1930).

[5] F. Horton, A. C. Davies, and U. Andrewes, *Proc. Roy. Soc.*, **117**, 649 (1928). We have tried various conducting glasses, but seldom have been able to make a resistor without polarization.

[6] L. C. Van Atta, *Rev. Sci. Instr.*, **1**, 687 (1930).

currents. Goetz[1] used a Hoffmann electrometer to study certain photoelectric properties of tin. The smallest detectable current was $\sim 10^{-18}$ amp (*i.e.*, six electrons/sec!). Steinke[2] expressed the sensitivity of his Hoffmann electrometer somewhat differently. A deflection of 1 mm (scale at 900 cm) corresponded to a charge of 2000 electrons (3.2×10^{-16} coul). A rate of deflection of 1 mm per minute would therefore mean a current of 5×10^{-18} amp. A method of registering the emission of individual photoelectrons, in a manner resembling that developed by Rutherford and Geiger for counting α-particles, was developed by Elster and Geitel.[3] A gas-filled alkali-metal cell was connected to a fiber-type electrometer. Just below that potential at which the glow discharge would start in the dark, it was noticed that the electrometer would charge up slowly by a series of small, irregularly spaced, discontinuous jumps. On exposing the cell to very faint light the frequency of the jumps increased. The frequency of the jumps, due to the light (obtained by subtracting the frequency in the dark), was found to be proportional to intensity of the light. These jumps record the escape of individual photoelectrons.

Rajewsky[3] detected the emission of single photoelectrons by means of a modified Geiger-Müller tube. The tube is lined with a suitable metal (Zn, Cd, etc., for the ultra-violet, or an alkali metal for the visible) and is

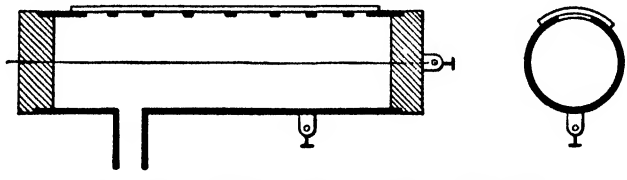


FIG. 12-16.—Photoelectric counter. (*Rajewsky.*)

provided with a glass or quartz window (Fig. 12-16). When the gas pressure and the voltage across the tube are correctly adjusted, an electrometer or amplifier connected to it (as in Fig. 2-17, page 35) records the emission of single electrons. When very feeble light is allowed to fall on the tube, it is found that the increase in the frequency of these emissions is proportional to the intensity of the light. (The electron emission in the dark is due to a variety of causes which cannot be avoided; photoelectrons are emitted in addition when the tube is illuminated.) Whereas

[1] A. GOETZ, *Phys. Rev.*, **33**, 373 (1929); G. HOFFMANN and W. S. PFORTE, *Phys. Zeits.*, **31**, 822 (1930); W. EGGERS, *Ann. d. Phys.*, **7**, 833 (1930); K. ENGEL and W. S. PFORTE, *Phys. Zeits.*, **32**, 81 (1931).

[2] E. STEINKE, *Zeits. f. Phys.*, **38**, 378 (1926).

[3] J. ELSTER and H. GEITEL, *Phys. Zeits.*, **17**, 268 (1916); B. RAJEWSKY, *Phys. Zeits.*, **32**, 121 (1931). See also Sec. **2-10**.

the minimum amount of (blue) light which Elster and Geitel could detect was 3×10^{-9} erg/cm²sec or 650 quanta/cm²sec, Rajewsky detected 9.1×10^{-11} erg/cm²sec or 12 quanta/cm²sec. This corresponds to about 20,000 times the highest sensitivity obtainable with the best photoelectric cells when connected to a quadrant electrometer and operated in the usual way. We thus have a powerful tool for investigating excessively feeble radiations, such for instance as the "mitogenetic" radiation which is said to be given off by certain roots.

Rajewsky does not give enough information to determine the photoelectric yield of his surface. The internal evidence in his paper suggests that he could detect with certainty the emission of four electrons per minute in addition to those spontaneously emitted, and if we assume that the area of his window was 5 cm², the yield is one electron to 900 quanta. This is far below the highest yields recorded (1 to 14, Sec. **5-10**). Consequently, if it were possible to use in Rajewsky's device, sensitized potassium surfaces, such as those giving the highest yields one might be able to measure light intensities well below 1 quantum/cm²sec in certain spectral regions![1]

12-15. Galvanometers.—The most sensitive suspended coil galvanometers can be used to detect currents as low as about 10^{-10} amp. (We give this merely as indicating the order of the lowest current detectable; some manufacturers have built special instruments whose performance exceeds this figure considerably, but their adjustment calls for patience.) For currents greater than 10^{-9} amp there are many robust, short-period galvanometers on the market, while for currents greater than 10^{-7} amp pointer-type instruments are available.

The minimum current detectable by a galvanometer can be extended to about 10^{-12} amp by means of Moll's thermo-relay.[2] It is probable, however, that the measurement of such currents could be effected with much less trouble by an electrometer combined with a resistance-shunt device.

In a simple circuit consisting of a photoelectric cell, a galvanometer, and a battery, it is desirable to have a protecting resistance of the order of 10,000 ohms in series. This is especially so with a gas-filled cell, as too high a voltage causes a glow discharge to pass, which, in the absence of sufficient resistance, might pass over into a destructive arc. A change in the photoelectric current passing through the protecting resistance alters the voltage drop across it, which in turn modifies the voltage available for the cell. If the cell be of the vacuum type this is seldom of any consequence, but if it be of the gas-filled type, working on the steep part of the current-voltage curve, such an effect makes it impossible to draw any quantitative conclusions as to the ratio of the light intensities falling

[1] See, however, footnote 2, p. 424.

[2] W. J. H. Moll and H. C. Burger, *Phil. Mag.*, **50**, 624 (1925). The thermo-relay is manufactured by P. J. Kipp and Zonen, Delft, Holland. Useful information will be found in their catalogue.

on the cell from the ratio of the corresponding photoelectric currents.[1,2] (This effect could be avoided by making use of a gas-filled photoelectric cell with two anodes—one screening the other—when the voltages are so chosen as to make a portion of the current-voltage curve practically flat.[2])

12-16. Amplification of Photoelectric Currents.—Although many papers have appeared from time to time describing amplifiers which, in principle, should rival sensitive electrometers in measuring very small currents, it is significant that physicists still prefer to use the electrometer in photoelectric investigations. Even as late as 1929, Campbell, on the basis of personal experience, concluded that the effective sensitivity of electrometers is decidedly greater than that of amplifiers. The effective sensitivity of the latter is limited by certain inherent irregularities in the radio tubes available. The situation, however, has been completely changed within the last year as a result of the development, by the General Electric Company, of a new tube with remarkable characteristics. Because of the immense advance in the steadiness and sensitivity of circuits containing these new tubes we shall limit ourselves principally to the discussion of such circuits.

The possibility of amplifying small photoelectric currents by means of the thermionic vacuum tube was recognized as early as 1916, and since then many types of amplifying circuits have been devised and used.[3] In fact, the present widespread use of the photoelectric cell in many commercial devices has been made possible only through the use of the thermionic amplifier, for the photoelectric currents themselves are in general so minute as to make them worthless as a commercial tool. However, while amplification methods have been extensively employed in commercial circuits, they have been but little used in the laboratory in the study of photoelectric problems. This is largely because in most commercial circuits (*e.g.*, sound pictures, television, etc.) the photoelectric currents are rapidly varying, usually at audio frequencies, so that the problem of amplification is identical with that of amplifying alternating currents, the technique for which has been developed on an elaborate scale in recent years. The investigator in photoelectricity, on the other hand, is primarily interested in the measurement of steady or slowly

[1] B. Kurrelmeyer, *Jour. Opt. Soc. Amer.*, **16**, 92 (1928).

[2] H. Geffcken and H. Richter, "Discussion on Photoelectric Cells," p. 102 (see footnote 1, p. 427).

[3] P. I. Wold, U. S. Patent 1,232,879, 1916; J. Kunz, *Phys. Rev.*, **10**, 205 (1917). An excellent account of the theory and technique of direct-current amplification has been given by W. B. Nottingham, *Jour. Franklin Inst.*, **209**, 287 (1930). For accounts of special circuits, see C. E. Wynn-Williams, *Proc. Camb. Phil. Soc.*, **28**, 810 (1927); *Phil. Mag.*, **6**, 324 (1928); J. M. Eglin, *Jour. Opt. Soc. Amer.*, **18**, 393 (1929); R. C. Dearle and L. A. Matheson, *Rev. Sci. Instr.*, **1**, 215 (1930); P. J. Razek and J. Mulder, *Jour. Opt. Soc. Amer.*, **18**, 460 (1929); **19**, 390 (1929); R. D. Bennett, *Rev. Sci. Instr.*, **1**, 466 (1930).

varying currents, and the problem of amplifying direct currents has not received so much attention.

The simplest type of circuit suitable for direct-current amplification is shown in Fig. 12-17. The current from the photoelectric cell is passed through a high resistance R and the potential drop across this resistance is impressed on the grid of a three-element tube. The change in the

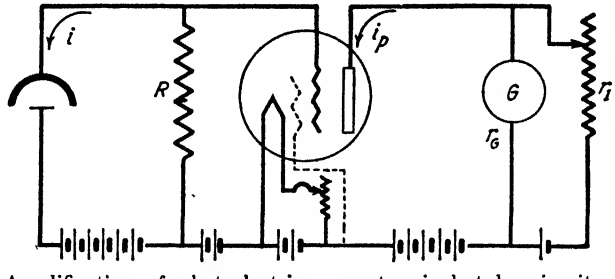


FIG. 12-17.—Amplification of photoelectric currents, single-tube circuit. (The dotted line represents the second grid in the FP-54 tube.)

potential of the grid produces a change in plate current which is registered on the galvanometer. By adjustment of the resistance r_1 the galvanometer can be made to read zero when the photoelectric current is zero, and only the *changes* in plate current are then observed. If the change in grid voltage is Δe_g and if the change in plate current produced is Δi_p, then,

$$\Delta i_p = \left(\frac{di_p}{de_g}\right)\Delta e_g = g_m \Delta e_g.$$

The factor di_p/de_g is characteristic of the tube, and is called the mutual conductance g_m. But Δi_p is the current registered by the galvanometer (if r_1 is much larger than r_G) and is equal to kD, where k is the sensitivity and D the deflection of the galvanometer. The voltage sensitivity S of the circuit then is

$$S \equiv \frac{D}{\Delta e_g} = \frac{g_m}{k}.$$

In ordinary radio tubes (such as the UX-201A) g_m is of the order of 800 microamp/volt and if the galvanometer sensitivity is, say, 10^{-8} amp/mm, then $S = 80{,}000$ mm/volt, which is considerably greater than can be easily attained with an electrometer. The circuit can be used, just like an electrometer, with a resistance shunt, using either a direct deflection or a null method (Sec. **12-13**). The current sensitivity will be, obviously,

$$S_i = \frac{D}{i} = \frac{D}{(\Delta e_g/R)} = \frac{Rg_m}{k},$$

where i is the photoelectric current passing through R. If $R = 10^7$ ohms, g_m/k remaining as before, $S_i = 8 \times 10^{11}$ mm/amp, which means a deflection of 1 mm for a current of 1.2×10^{-12} amp.

Now, it will be seen that the *voltage* sensitivity can be increased by increasing the sensitivity of the galvanometer (decreasing k), while the *current* sensitivity may be increased by increasing R as well. However, with ordinary tubes these cannot be increased much beyond the values given above because: (1) there will always be a natural unsteadiness of the plate current due to slight irregular changes in battery voltages, and other causes, and these will produce irregular fluctuations in the galvanometer if one with too high sensitivity is used; and (2) it is useless to continue to increase R, since it is always shunted by the grid-to-filament resistance within the tube itself, which in most tubes is not larger than about 10^8 ohms.

For many years these two factors have put a serious limit upon the usefulness of radio tubes in the amplification of very small currents. However, very recently, Hull, Metcalf, and Thompson,[1] of the General Electric Laboratories, have developed a new type of four-element tube (the FP-54 pliotron) in which all sources of current to the control grid within the tube have been either eliminated or greatly reduced, so that the effective grid-to-filament resistance has been increased to the order of 10^{15} ohms.[2] The limitation set by 2, above, is therefore reduced by a factor of 10^7. At the same time the tube is designed to operate on a total voltage of 12 volts, thus allowing the use of large storage batteries, which are inherently steadier than the smaller "B" batteries hitherto necessary for providing the higher voltages. These tubes may be used in the circuit shown in Fig. 12-17, by providing a tap in the plate battery for the fourth element, which is a space-charge grid operated at a small positive potential. With this arrangement, satisfactory measurements can be made of currents as small as 10^{-13} or 10^{-14} amp. Where smaller currents are to be measured, or where great stability and precision are desired, it is necessary further to eliminate the effects of battery fluctuations. This can be accomplished by using the circuit shown in Fig. 12-18, which has often been employed with ordinary tubes. In this circuit two tubes are used and it is possible to balance the circuit so that the galvanometer is unaffected by small changes in the battery voltages. With such a circuit a stable voltage sensitivity of 250,000 mm/volt may be obtained with the new FP-54 tubes.[3] With $R = 10^{11}$

[1] G. F. Metcalf and B. J. Thompson, *Phys. Rev.*, **36**, 1489 (1930).

[2] These new tubes have a mutual conductance of about 25 microamp/volt, hence a voltage sensitivity of 80,000 mm/volt can be attained with a galvanometer whose sensitivity is 10^{-10} amp/mm.

[3] We have been informed by several investigators that they have found it impossible to attain steady voltage sensitivities as high as this, owing to the fact that the tubes purchased from the manufacturers were not sufficiently well matched to allow accurate balancing. In the investigation reported by DuBridge (footnote 1, page 448) specially matched tubes were available.

ohms there will be a deflection of 1 mm for a photoelectric current of 4×10^{-17} amp. Alternatively, R can be made infinite and the rate of deflection observed as with an electrometer. Since the capacity of the grid is only of the order of 3 e.s.u., it has been found possible by this method to detect a current of 5×10^{-18} amp.[1]

If in place of the galvanometer another stage of amplification is used, employing ordinary power amplifier tubes (such as the UX-112A),

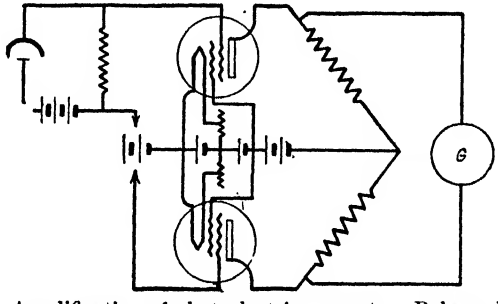


FIG. 12-18.—Amplification of photoelectric currents. Balanced-tube circuit.

then an output current of 1 microamp may be obtained for an input photoelectric current of 10^{-13} amp—an amplification of 10^7 times.[1]

It is evident then that relatively simple amplification circuits can now be constructed whose sensitivity is exceeded only by that of the Hoffman electrometer. The advantages of using amplification are:

1. It is possible to use as a measuring instrument a rugged and easily handled galvanometer in place of a rather delicate electrometer.

2. For a given voltage sensitivity the amplification circuit will be both electrically and mechanically more stable than an electrometer.

3. Comparing an electrometer with an amplifier of equal stability, the latter will have the greater voltage sensitivity; hence, instead of the rate-of-charge method, the more convenient and precise steady-deflection method, using a high-resistance shunt, may be employed.

12-17. Balance Methods.—In most of the applications of photoelectric cells we are really concerned, directly or indirectly, with a measurement of light intensity as indicated by a photoelectric current arising from the light. In principle this should be a simple matter, for one of the most firmly established laws of photoelectricity is that the number of photoelectrons is exactly proportional to the intensity of the light used, provided that the properties of the surface are not altered in any way. In practice, however, we find many photoelectric cells in which the observed photoelectric current is not strictly proportional to the light intensity, and in which, for a given light intensity, the current changes with the age of the cell. It is therefore unsafe to say that the intensities

[1] For a more detailed account of the results obtained with the new tubes, see L. A. DuBridge, *Phys. Rev.*, **37**, 392 (1931).

of different illuminations,[1] incident at different times on the photoelectric cell, will always be strictly proportional to the currents measured by the galvanometer. There are at least two arrangements whereby this uncertainty can be avoided.

a. Balancing of Two Photoelectric Cells.—Two photoelectric cells (preferably with similar characteristics) are connected as shown in Fig. 12-19. It will be seen that the photoelectric currents from the two cells pass through the indicator I in opposite directions. This indicator may be (1) a galvanometer, (2) an amplifier actuating a pointer galvanometer, or (3) an electrometer. The stronger illumination is now cut down by a suitable "intensity reducer" (which will be discussed at the end of this section) until the photoelectric currents are equal. The ratio of the original intensities is evidently given by the reading of the intensity reducer. An example of the application of this method will be found in Sec. **13-5**.

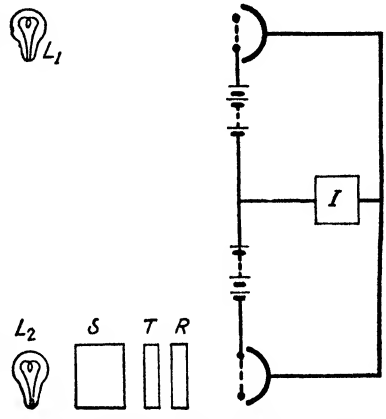


FIG. 12-19.—Balancing of photoelectric currents (schematic representation). L_1, L_2, lamps on same battery. S, filter or monochromator. R, intensity reducer. T, sample whose transmission is being measured.

b. Equal Deflection Method.—All troubles arising from the deviations of the characteristics of photoelectric cells from the ideal can be obviated if we throw the beams of light, whose intensities we wish to compare, alternately on to a photoelectric cell, and cut down the stronger light by means of a suitable intensity reducer until both beams produce equal photoelectric currents in the cell. The characteristics of the cell are now immaterial, for we may certainly assume that equal light intensities will produce equal photoelectric currents and that is all that is necessary.[2] In some investigations the currents due to the two sources are observed separately. In other investigations, suitable mechanical devices alternate the illuminations rapidly and the inequality of the corresponding photoelectric currents is detected by one of the several possible arrangements for detecting pulsating currents. (This second method has the advantage over the first that there is less opportunity for any change to occur in the photoelectric cell between successive illuminations.) Practical applications of both methods are found in Sec. **13-3** and **13-5**.

[1] It is to be assumed, of course, that the illuminations are of identical spectral composition.

[2] An additional refinement, which might be necessary with certain cells, would be to require that the two beams have the same area and the same intensity distribution over that area.

Here, as in *a*, the ratio of the original light intensities is determined by the "reading" of the intensity reducer. The characteristics of the photoelectric cell and its circuit are unimportant; all that is asked of them is to give the same current for the same illumination over a short period. Consequently, the accuracy of the measurements depends on the working of the device for reducing the intensity of the light by a definite amount. We shall therefore consider various types of intensity reducers.

c. Intensity Reducers.—The reduction of the intensity of one of the beams until it is equal to that of the other may be effected by one of the following devices:

1. Adjustable rotating sector.
2. Set of grids with different transmissions.
3. Set of gray filters with different transmissions.
4. Neutral gray wedge.
5. Ditchburn's rotating sector.
6. Movable source (application of the inverse square law).
7. Pair of Nicol prisms.

The rotating sector 1 merely lowers the average illumination, for what it does is to alternate full illumination and zero illumination in rapid succession. The rotating sector "cannot be used unless Talbot's law is true, *i.e.*, unless the time average of the photoelectric current is determined wholly by the time average of the incident light. The law is always true if the current is proportional to the light, and sometimes when it is not."[1] In Gibson's arrangement[2] one lamp could be moved back and forth along a photometer bench allowing method 6 to be used as a check on method 1. Since the reduction obtained by devices 2 and 3 is in finite steps, interpolation is necessary. As to 3 and 4, "gray" filters and wedges are made in gelatin by the Eastman Kodak Company and in glass by certain other manufacturers. They are seldom truly neutral, but a calibration curve enables one to allow for this feature. The transmission through a pair of Nicol prisms is proportional to the square of the cosine of the angle between their corresponding planes. Ditchburn's sector is an adjustable V-shaped opening in a disk which is mounted between two lenses so placed between the source and the cell that the light rays are all parallel to the axis in the region between the lenses.[3] If the conditions were ideal, there would be no need to rotate the sector; in practice, however, the finite size of the source and other deviations from ideal conditions make it necessary. As the purpose of rotation is merely to

[1] N. R. Campbell and Dorothy Ritchie, "Photoelectric Cells," p. 193 (Sir Isaac Pitman & Sons, 1929); also G. H. Carruthers and T. H. Harrison, *Phil. Mag.*, **7**, 792 (1929); **8**, 64 (1929); W. S. Stiles, *Phil. Mag.*, **7**, 812 (1929); G. H. Carruthers; *Phil. Mag.*, **8**, 210 (1929); N. R. Campbell, *Phil. Mag.*, **8**, 63 (1929).

[2] K. S. Gibson, *Jour. Opt. Soc. Amer.*, **7**, 693 (1923).

[3] R. W. Ditchburn, *Proc. Camb. Phil. Soc.*, **23**, 959 (1927).

even out minor inequalities, departures from Talbot's law have a negligible effect.

12-18. Campbell's Use of Intermittent Currents.—If the voltage across a gas-filled cell be increased sufficiently, a glow discharge will appear, regardless of whether the cell is illuminated or not. The conditions for the appearance of a glow discharge are usually absent from most arrangements in which a photoelectric cell is used. Campbell,[1] however, makes use of the glow-discharge phenomenon in a gas-filled photoelectric cell in a most ingenious way. The cathode C of a photoelectric cell is connected to the plate P of a current-limiting kenotron (Fig. 12-20). If a

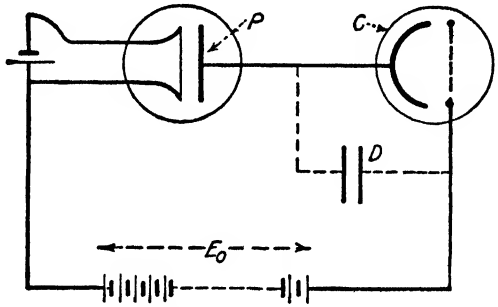


FIG. 12-20.—Photoelectric cell with kenetron. (D is a condenser of small capacity to control frequency of intermittence.)

voltage E_0 be applied across the tube and cell, and the filament be heated to allow a current to flow, the voltage across the cell will build up almost to E_0 if there be no light incident on the cell. If, however, E_0 is greater than E_1 (the voltage at which the glow discharge sets in), the discharge will begin when the voltage reaches E_1, and will continue so long as it exceeds the stopping potential E_1' for the discharge. The glow discharge will continue so long as the kenotron provides enough current. If it does not, the discharge will cease and the whole cycle will begin over again, thus leading to an intermittent glow discharge.

In Fig. 12-21 the curve CB represents the glow characteristic, which, in this photoelectric cell, cannot exist below 185 volts. EDA is the voltage-current characteristic of the cell with a given illumination. As the voltage is stepped up to 210 volts (for this particular cell) the current passes over into a glow discharge, illumination being no longer necessary. If the kenotron does not allow a current greater than X to pass, then, as we raise the voltage, the current through the illuminated cell cannot exceed X and so the representative point will be on EDA. If the kenotron permits a current *greater* than Y to pass, the photoelectric current will build up rapidly along EDA and at A it will pass over dis-

[1] N. R. CAMPBELL, *Phil. Mag.*, 3, 1041 (1927); N. R. CAMPBELL and DOROTHY RITCHIE, "Photoelectric Cells," Chaps. VII and XII (Sir Isaac Pitman & Sons, 1929).

continuously into the glow discharge, the permanent current being that transmitted by the kenotron. If, however, the current permitted by the kenotron has a value between X and Y, we shall find the current oscillating discontinuously between two sets of values, the representative point traversing the cycle $ABCD$. The intermittency can be detected by a telephone receiver or some equivalent device in the circuit.

Now the maximum photoelectric current which can be carried by the cell, without it passing over into a glow discharge, depends somewhat on the illumination (*e.g.*, i_1 for weak light and i_1' for strong light [Fig.

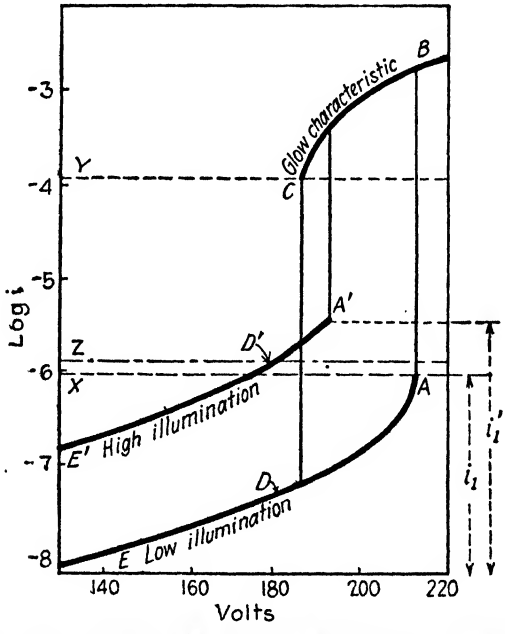


FIG. 12-21.—Characteristics of a gas-filled cell. (*Campbell.*)

12-21]). If the kenotron permits a current Z to pass, then, with low illumination, we shall have, as before, the cycle $ABCD$ traversed. But if the illumination be increased so that the photoelectric voltage-current characteristic is now $E'D'A'$, the limitation of the current by the kenotron does not allow the representative point to move beyond D', and this consequently represents the steady current obtained. There is now no intermittent effect.

The practical application of these effects is due to the fact that it is possible to stop the intermittent glow discharge by raising the intensity of the light to a critical value. Alternatively, when light of a given intensity produces a continuous glow discharge, a diminution in intensity to a critical value will introduce intermittency. The circuit when connected through a suitable amplifier to a relay has obvious applications (*e.g.*, turning on lights when daylight falls below a certain level). While this method is not directly quantitative since the intensity of a beam cannot be measured by the

effect produced, it can be used as an indicator to tell when the intensity has been reduced to the critical value to stop (or start) intermittency.[1] Thus the intensities of two beams can be compared by their readings on a suitable intensity reducer—the device being used merely to find out when the reduced beams are equal. Further details will be found in the publications cited. It is claimed that the kenotron-photoelectric-cell combination has a very wide range of application and, besides being extremely simple and robust, is very sensitive.

CONCERNING LIGHT IN PHOTOELECTRIC EXPERIMENTS

In experiments on the photoelectric effects of illuminated surfaces, precise knowledge as to the spectral distribution and intensity of the light is frequently of great importance. We shall, therefore, discuss briefly the various sources of light which have been found useful in photoelectric experiments, monochromators and filters for isolating spectral bands, and methods of measuring light intensity.

12-19. Sources of Light for Photoelectric Experiments.—For investigations in the visible and infra-red, the carbon arc and gas-filled tungsten lamp are very suitable. Provided that extremely high illumination is not required, a tungsten lamp operated by a steady voltage leaves nothing to be desired in the way of constant illumination. Should stronger monochromatic light be required than can be obtained by means of a tungsten lamp and a monochromator, it is possible to use a mercury lamp (or some other source of line spectra) in combination with certain selected filters (see Sec. **12-21** and Table 12-4, page 457).

Though no applications to photoelectric experiments have been made, it should be possible to obtain strong, practically monochromatic yellow light by spraying a flame with salt solution, or by passing a discharge through a tube containing hydrogen and metallic sodium (Langer).[2] It might be necessary to use a suitable filter to remove undesired lines. (The same methods should give light of wave-lengths 7668A and 7702A on substituting potassium for sodium.)

The most convenient source of light in the ultra-violet is the quartz mercury lamp.[3] Several excellent commercial types are available (Cooper-Hewitt, Hanovia, etc.). By constricting the quartz tube in which the arc takes place to between 2 and 4 mm, and by operating at a much higher wattage than usual, several investigators have been able to increase the surface brightness very greatly.[4] Thus in Hulburt's form of mercury lamp the surface brightness was 500 times that of the

[1] A finer criterion is the *change* in the frequency of intermittence due to small changes in the light intensity.

[2] Private communication.

[3] Good summaries of the characteristics of mercury lamps are given by L. J. Buttolph in *Bulletins* 104*A* and 105*B*, issued by the Cooper-Hewitt Electric Company (now the General Electric Vapor Lamp Company).

[4] G. S. Forbes and G. R. Harrison, *Jour. Opt. Soc. Amer.*, **11**, 99 (1925); E. O. Hulburt, *Phys. Rev.*, **32**, 593 (1928); L. Dunoyer, *Rev. d'Opt.*, **6**, 328 (1927); E. L. Harrington, *Phil. Mag.*, **4**, 836 (1927).

convenient Cooper-Hewitt "Lab-Arc." The emission of light from some mercury lamps has been found to decrease after many hours of operation owing to the formation of a film of some sort on the inside of the quartz tube. The effect is especially marked for the shorter wave-lengths (< 2700A).[1] The energy available in the spectrum of the mercury lamp[2] in the range 1850A to 2360A is about equal to that in the range 2360A to 2500A and about one-fiftieth of that in the range 4000A

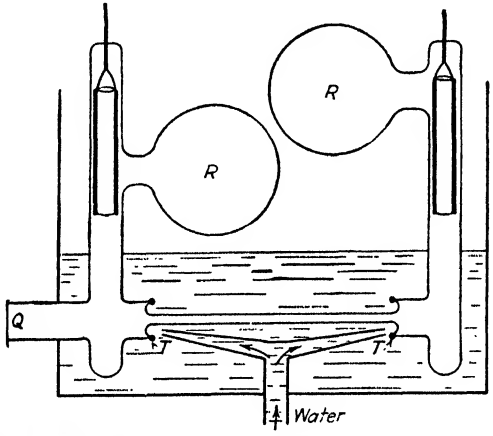


FIG. 12-22.—Hydrogen-discharge tube. Q, quartz window to transmit ultra-violet light. T, water jets cool cemented junctions of quartz to glass. R, gas reservoirs (actually much larger).

to 4500A. The iron arc has been used with success when a mercury lamp does not give enough light, especially in the short wave-length region.

Various investigators have used a strong discharge through hydrogen as an intense source of (practically continuous) ultra-violet light. The arrangement developed by Lawrence and Edlefsen (Fig. 12-22) is typical of the arrangements used by the others; it uses the greatest amount of power (6.5 amp, 3000 volts).[3] This hydrogen discharge is especially rich in the short wave-length region (< 2500A) and probably gives out much more light in all regions of the spectrum than the other sources already discussed.

The new Sunlight Mazda Lamp (S-1), developed by the General Electric Company, may prove to be a very useful source of light in photoelectric experiments. It is essentially a mercury arc between tungsten electrodes, consuming about 300 watts. While it gives less total light than ordinary mercury arcs in quartz, the greater concentration of the light may in some cases be an advantage. Although the bulb contains argon as well as mercury, only the mercury spectrum appears on a continuous

[1] A. E. GILLAM and R. A. MORTON, *Phil. Mag.*, **6**, 1123 (1928); W. MEYN, *Zeits. f. Wiss. Photog.*, **25**, 345 (1928).

[2] See also Sec. **12-22**.

[3] RAYLEIGH, *Proc. Roy. Soc.*, **117**, 294 (1927); Z. BAY and W. STEINER, *Zeits. f. Phys.*, **45**, 337 (1927); E. O. LAWRENCE and N. E. EDLEFSEN, *Rev. Sci. Instr.*, **1**, 45 (1930).

background. The special glass bulb used ceases to transmit appreciably in the neighborhood of 2500A.[1]

12-20. Monochromatic Illuminators.—A monochromator, or monochromatic illuminator, is a modification of a spectrograph, designed to isolate narrow regions of the spectrum. In principle, a slit takes the place of the photographic plate and is moved across the spectrum, or (what is far more common) the slit is fixed and the spectrum made to move across it. The desiderata are two: (1) great light gathering power, and (2) spectral purity of the isolated light. The former is achieved by means of lenses of large aperture-to-focus ratios, and generally large over-all dimensions. The latter is promoted by properly diaphragming the telescope and collimator tubes, and keeping the surfaces of the lenses and prisms clean. Unfortunately, however, some degree of impurity seems unavoidable. This is easily demonstrated by observing the spectrum of the light transmitted by a monochromator set to transmit a certain line, *e.g.*, 5461A, from a mercury arc. It will be found that, in addition to the line which the instrument is supposed to transmit, all the other lines in the spectrum will appear faintly. In certain experiments, particularly those on thresholds, this may give spurious results owing to the presence of feeble radiation of shorter wave-lengths than that which one is supposed to be using. This effect may be much diminished by using with the monochromator a filter having a "cut-off" on the short wave-length side of that wave-length which one desires to use, so that all shorter wave-lengths are suppressed. (Cut-off filters are listed in Sec. **12-21.**)

The double monochromator has been designed to improve the purity of the transmitted light. It is, in effect, merely two single monochromators put end to end in one instrument, so that if the admixture of undesired light is, say, 1:100 in each, then in the double monochromator it should be 1:10,000.

Monochromators are generally made in quartz to allow working in the ultra-violet. Some are made in glass; these should be used when the small dispersion of the quartz instruments does not give enough resolution in the visible. Single monochromators are made by Bausch and Lomb, Gaertner, Hilger, Leiss, Zeiss, and Steinheil. Double monochromators are made by Kipp, Leiss, and Spindler and Hoyer.

The percentage of light transmitted by monochromators has been determined by Anderson, Frazer and Bird, and by Forsythe and Barnes.[2] The former obtained values ranging from 19 per cent at 2500A to 9 per cent at 4000A, while the latter obtained values ranging from 48 per

[1] W. E. Forsythe, B. T. Barnes, and H. A. Easley, *Jour. Opt. Soc. Amer.*, **21**, 30 (1931); A. H. Taylor, *Jour. Opt. Soc. Amer.*, **21**, 20 (1931); D. Dooley, *Phys. Rev.*, **36**, 1476 (1930).

[2] W. T. Anderson, H. D. Frazer, and L. F. Bird, *Jour. Opt. Soc. Amer.*, **17**, 454 (1928); W. E. Forsythe and B. T. Barnes, *Rev. Sci. Instr.*, **1**, 569 (1930).

cent at 6000A and 43 per cent at 4000A to 24 per cent at 2500A. Inasmuch as the monochromators were in each case made to the design of the respective authors, agreement could not be expected. It is rather surprising, however, to find that in one case the transmission increases as we go along the spectrum, while in the other case it does the opposite.[1]

12-21. Filters and Reflectors.—Light filters are used in photoelectric investigations in two ways—to isolate narrow regions of the spectrum, or to cut off light of a shorter wave-length than that of a certain desired value. In the first case it may be possible to find sources giving widely spaced spectral lines, so that in combination with a suitable filter only one line will be transmitted. Such a source and filter may give far greater intensity than can be obtained by means of a monochromator. In Table 12-4, we list sources which, when combined with appropriate filters, give approximately monochromatic light. In some cases a high degree of purity can be obtained.

A list of filters arranged according to their short wave-length cut-offs is given in Table 12-5. Such filters may be useful (*a*) in improving the purity of light isolated by a monochromator by cutting out the light on the short wave-length side of that which the instrument is set to transmit, and (*b*) in experiments in which all that concerns us is the shortest effective wave-length. The most desirable cut-off filters are those with a steep absorption curve in which the change from high transmission to practically complete absorption is effected in as short a range as possible. (A filter is seldom found in which the transmission changes from 50 per cent to 1 per cent or less in 200A.) The wave-length given in the first column (Table 12-5) is that at which the filter ceases to transmit appreciably; when data are available it is the wave-length at which the transmission is less than 1 per cent. The table has been compiled from a variety of published researches in which the details furnished and the precision of the measurements differ widely; this should be remembered when making use of the results. Whenever possible, a test of the transmission of any filter that it is proposed to use should be made. More information about filters will be found in the publications cited in the table, particularly numbers 1, 2, 3, 4 and 7. Full details concerning the transmission of a remarkably useful series of gelatine filters made by the Eastman Kodak Company will be found in their booklet.[2] Quantitative results as to the transmission of a large number of materials are tabulated in the "International Critical Tables" by Gibson (Volume V, pages 271–274) and by Henri (Volume V, pages 359–379).

[1] Since this section was written, a new type of monochromator has been described by C. Leiss in a paper entitled "A New Vacuum Double Monochromator for Wave-lengths down to 1300A," (*Zeits. f. Phys.*, **68**, 559 [1931]).

[2] "Wratten Light Filters," published by the Eastman Kodak Company.

TABLE 12-4.—SOURCES OF MONOCHROMATIC LIGHT

Wave-length isolated	Source	Filter (C) Glass made by the Corning Glass Company (see footnote 4) (EK) Wratten gelatine made by the Eastman Kodak Company	Per cent transmitted	Purity (No inf. = no information)	Reference
10,829A	Hg arc	(C) Code 255, 7 mm	Large	No inf.	1
10,140A	He discharge	(EK)88 or 87	80	No inf.	2
				A 20-mm water cell diminishes infra-red beyond 13,800A	3
7,065A	He discharge	(C) Code 243, 6 mm, and Code 506, 5.6 mm	36	No inf. as to long λ side; sharp cut-off on short λ side	4
6,678A	He discharge	(C) Code 242, 6 mm	70	7065A transmitted. No inf. as to long λ side, sharp cut-off on short λ side	4
6,563A	H discharge	(C) Code 243, 6 mm	66	Pure (if the molecular spectrum be suppressed)	4
5,769A	Hg arc	(C) Code 348, 3.5 mm	75	Weak lines 6152A and 6232A present and a trace of 5461A	1
5,791A		(EK)22	70	Weak lines 6152A and 6232A present, no shorter λ's	2
5,461A	Hg arc	(C) Code 512, 9 mm, and Code 351, 3.5 mm	35	Pure	1
		(EK)62	12	Pure	2
		(EK)77	72	0.5 per cent of 5791A and 5769A	2
		(EK)77A	68	Pure	2
4,862A	H discharge	(C) Noviol B, 3 mm, and Code 440, 5.5 mm	38	Pure (if the molecular spectrum be suppressed)	4
4,359A	Hg arc	(C) Noviol A, 3 mm, and Code 585, 4 mm	22	Pure	1
		(EK)50	14	0.4 per cent of 4047A and 4078A	2
4,341A	H discharge	(C) Noviol A, 2 mm, and Code 585, 4.6 mm	27	Pure (if the molecular spectrum be suppressed)	4
4,047A	Hg arc	(C) Code 597, 4 mm, and Code 306, 3.5 mm	6	Pure	1
4,078A					
3,889A	He discharge	A nickel oxide glass	"Very large"	Trace of 3965A and 4025A	5
		(C) Red purple ultra and Code 512, or quinine sulphate	30(?)	Trace of 3965A and 4025A	6,4
3,650A	Hg arc	(C) Code 586, 9 mm	38	10 per cent of 3342A to 3352A.	1
3,656A					
3,663A		(C) Code 597, 3.2 mm, and 10 per cent $CuSO_4$ solut., 20 mm	69	No shorter λ's; transmitting to 4300A on long λ side	3
3,126A	Hg arc	Silver film sputtered on quartz	50	No other lines; width of transmission band 3050A to 3350A	7
3,132A					
2,536A	Hg arc	Chlorine at 6 atmos. in cell, 4 cm long, and thiophene	(?)	2654A to 4359A absorbed; thiophene cuts off λ's shorter than 2536A	8

[1] *Bulletins* 104*A* and 105*A*, published by the Cooper-Hewitt Electric Company.
[2] "Wratten Light Filters," published by the Eastman Kodak Company.
[3] L. A. JONES, *Jour. Opt. Soc. Amer.*, **16**, 259 (1928).
[4] K. S. GIBSON, E. P. T. TYNDALL, and H. J. MCNICHOLAS, *U. S. Bur. Standards, Tech. Paper*, No. 148 (1920). Note: The names of the various Corning glasses as given in this paper are no longer in use. We have therefore designated each glass by the Code Number under which it is now listed by the Corning Glass Company.
[5] R. W. WOOD, *Phil. Mag.*, **7**, 858 (1929).
[6] Data furnished by the Corning Glass Company.
[7] E. PETTIT, *Astrophys. Jour.*, **66**, 43 (1927); RAYLEIGH, *Proc. Roy. Soc.*, **128**, 131 (1930).
[8] O. OLDENBURG, *Zeits. f. Phys.*, **29**, 328 (1924).

TABLE 12-5.—SHORT WAVE CUT-OFF FILTERS

Cut-off	Material (C) Corning Glass (see footnote 4) (EK) Wratten gelatine filters made by Eastman Kodak Company	Thickness, etc.	Comments	Reference
900A 1230A	Thin celluloid Clear fluorite	30 to 40 mμ 1 to 2 mm	Gradual cut-off. Only very occasional specimens transmit as far as this	9,10 10
1450A	Clear quartz (crystalline)	0.2 mm	Different specimens have practically identical transmission limits	10
1500A	Clear quartz (crystalline)	2 mm	Air paths have strong absorption below this point	10
1600A	Clear quartz (crystalline)	20 mm		10
1700A	Oxygen in a quartz (crystalline) cell	10 mm, at atmos. pressure		10
1750A	Water in a quartz (crystalline) cell	20 mm	Steep cut-off. (Lyman finds, however, that 0.5 mm of water has a sharp cut-off at 1729A)	1,10
1750A	Clear fused quartz	0.3 mm	Transmissions: 1849A, 24 per cent 1971A, 36 per cent 2002A, 40 per cent	12
1850A	Quartz mercury lamp		1850A is the shortest wavelength emitted by a new lamp	
2000A	Clear fused quartz	3.0 mm	Transmissions: 2000A, 0 per cent 2100A, 56 per cent (Different specimens vary widely in transmission)	13
1900A 2000A	Acetic acid in water Acetic acid in water	32 mm, 1 part acid in 1000 parts water 32 mm, 1 part acid in 200 parts water	The concentrations are merely rough estimates; it is best to find by trial the desired concentration	11
2200A	(C) Code 970	5 mm	Gradual cut-off; ("solarizes" with short λ's)	6
2200A	Calcite	10 mm		14,15
2300A	Rocksalt	12 mm	Lyman and Pfluger, however, found rocksalt to transmit as far as 1750A	15 10
2350A	p-Dichlorobenzene	50 mm; satur. solut. in water		16
2450A	Tartaric acid	3.2 mm; 1 part satur. solut. in 64 parts water		17

TABLE 12-5.—SHORT WAVE CUT-OFF FILTERS.—(*Continued*)

Cut-off	Material (C) Corning Glass (see footnote 4) (EK) Wratten gelatine filters made by Eastman Kodak Company	Thickness, etc.	Comments	Reference
2500A	Thiophene	50 mm; satur. solut. in water	Steep cut-off	16,18
2800A	Benzol		Steep cut-off	7
2800A	(C) Code 971	2.1 mm	Fairly steep cut-off	6
2900A	(C) Code 971	4.9 mm	Fairly steep cut-off	6
3000A	(C) Pyrex	1.0 mm		4
3000A	Potassium-hydrogen phthalate	1.0 mm one-fifth molar aqueous solut.	Steep cut-off	18
3400A	Mirror glass (Bausch and Lomb)	20 mm		4
3600A	Quinine sulphate	10 mm; 3 mg/cc in water	Steep cut-off	7
4100A	(C) Noviol A	2 mm	Steep cut-off	4
4400A	(C) Noviol B	3.2 mm	Steep cut-off	4
4500A	(EK)4		Steep cut-off	2
4600A	(C) Code 351	3.04 mm		4
4700A	(C) Code 351	6.00 mm		4
5100A	(C) Code 349	1.13 mm		4
5200A	(EK)16		Steep cut-off	2
5300A	(EK)21			2
5600A	(EK)23		Steep cut-off	2
5800A	(EK)25			2
6000A	(C) Code 243	0.9 mm		4
6000A	(EK)29			2
6200A	(C) Code 243	6.0 mm		4
6500A	(EK)89			2
6800A	(EK)89A			2
7200A	(EK)88A			2

[1] to [8] See footnotes of Table 12-4.

[9] E. R. LAIRD, *Phys. Rev.*, **15**, 543 (1920); **29**, 41 (1927).

[10] T. LYMAN, "The Spectroscopy of the Extreme Ultra-Violet" (Longmans, Green & Co., 1928).

[11] L. A. DUBRIDGE, *Phys. Rev.*, **29**, 451 (1927).

[12] A. L. HUGHES, unpublished.

[13] G. JOOS, *Phys. Zeits.*, **25**, 376 (1924).

[14] A. PFLÜGER, *Phys. Zeits.*, **5**, 215 (1904).

[15] P. WRIGHT, *Brit. Jour. Radiol.*, **2**, 434 (1929).

[16] T. M. DAHM, *Jour. Opt. Soc. Amer.*, **15**, 266 (1927).

[17] R. C. WILLIAMSON, *Phys. Rev.*, **21**, 110 (1923).

[18] F. SAUNDERS, *Jour. Opt. Soc. Amer.*, **16**, 362 (1928).

A knowledge of the reflecting power of substances may occasionally be required. While many metals have a high reflecting power in the visible, it usually falls to a relatively low value in the ultra-violet. The reflecting power of silver is abnormally low in the vicinity of 3100A. According to Hulburt,[1] the best reflector for the region 1850A to 3800A is silicon. It is, however, impossible to make large optically flat reflecting surfaces out of it. The next best substances are nickel, stellite, and platinum. The best reflectors in the region 1600A to 1800A are platinum, chromium, and nickel (which reflect between 10 and 30 per cent).[2]

12-22. Spectral Energy Measurements.—In studying the color sensitivity curves for photoelectric surfaces, or in determining their photoelectric thresholds, it is necessary to plot a curve of the photoelectric current excited by unit intensity of incident monochromatic light as a function of the wave-length. This "spectral distribution curve" represents what the photoelectric response of the surface would be to an "equal energy spectrum," *i.e.*, one in which each equal wave-length range carried the same energy. Since an equal energy spectrum is unattainable in practice it is necessary to determine the distribution of energy among the various wave-lengths for the particular source used.

More precisely, if $E(\lambda)d\lambda$ be the energy radiated by the source in the wave-length range $d\lambda$ at λ, and if $f(\lambda)d\lambda$ is the photoelectric current excited by this radiation, then the spectral distribution function is defined as the ratio, $f(\lambda)/E(\lambda)$. We shall indicate briefly in this section the experimental methods for determining $E(\lambda)$.

An ideal procedure would be of course to use as a source of light a "black body" at a known temperature T, for which $E(\lambda)$ could be computed from the Planck radiation law,

$$E(\lambda) = \frac{c_1}{\lambda^5} \frac{1}{e^{\frac{c_2}{\lambda T}} - 1}.$$

If $E(\lambda)$ is taken to be the energy radiated per second per unit solid angle in a direction normal to unit area of the black-body emitting surface, then the universal constants c_1 and c_2 are given by,[3]

$$c_1 = 2hc^2 = 11.78 \times 10^{-6} \text{ erg/sec cm}^2,$$

$$c_2 = \frac{hc}{k} = 1.433 \text{ cm deg.}$$

For temperatures below 3000°K and wave-lengths shorter than 7000A (and hence for all ordinary measurements of the type being discussed in this section) an error of less than 0.1 per cent is made if the Wien radiation law is used in place of Planck's. Then

[1] E. O. Hulburt, *Astrophys. Jour.*, **42**, 205 (1915).

[2] P. R. Gleason, *Proc. Nat. Acad. Sci.*, **15**, 551 (1929).

[3] W. W. Coblentz, "International Critical Tables," Vol. V, p. 237 (McGraw-Hill Book Company, Inc., 1929).

$$E(\lambda) = \left(\frac{c_1}{\lambda^5}\right)e^{-\frac{c_2}{\lambda T}},$$

where the symbols have the same significance as before. A complete tabulation of numerical values of $E(\lambda)$ as a function of λ and T is given in the "International Critical Tables."[1]

In practice, of course, it is more feasible to use, instead of an actual black body, a tungsten filament operated at a suitable temperature. The values of $E_w(\lambda)$ can be obtained from those given for a black body by multiplying by the emissivity[2] of tungsten for the temperature and wave-length in question. We record below in Table 12-6 a set of values for $E_w(\lambda)$ for a tungsten radiating surface at several temperatures. The values as plotted in the form $\log_{10}E_w$ vs. $1/\lambda$ (Fig. 12-23) will be found useful for interpolations. In practice the intensity of radiation at various wave-lengths, transmitted from the source through a monochromatic illuminator, will be proportional to these numbers only if the wave-length range $d\lambda$ of the transmitted light is kept fixed by suitable adjustment of the width of the exit slit, and if correction is made for the absorption in the instrument itself.

TABLE 12-6.—SPECTRAL DISTRIBUTION OF THERMAL RADIATION FROM TUNGSTEN

λ A.u.	$E_w(\lambda)$ (watt/cm³)			
	2000°K	2500°K	2800°K	3000°K
2000	5.62×10^{-5}	7.15×10^{-2}	1.442	8.32
2500	2.31×10^{-2}	7.03	7.59×10^{1}	3.15×10^{2}
3000	1.08	1.25×10^{2}	9.20×10^{2}	2.98×10^{3}
3500	1.47×10^{1}	8.69×10^{2}	4.27×10^{3}	1.31×10^{4}
4000	9.51×10^{1}	3.36×10^{3}	1.50×10^{4}	3.59×10^{4}
4500	3.78×10^{2}	8.93×10^{3}	3.38×10^{4}	7.31×10^{4}
5000	1.08×10^{3}	1.84×10^{4}	6.07×10^{4}	1.22×10^{5}
5500	2.39×10^{3}	3.14×10^{4}	9.40×10^{4}	1.76×10^{5}
6000	4.50×10^{3}	4.76×10^{4}	1.29×10^{5}	2.30×10^{5}
6500	7.40×10^{3}	6.52×10^{4}	1.64×10^{5}	2.76×10^{5}
7000	1.10×10^{4}	8.27×10^{4}	1.93×10^{5}	3.15×10^{5}

NOTE.—$E_w(\lambda)$ is the rate of emission of energy in watts, from 1 cm² of surface, in a direction perpendicular to the surface, per unit solid angle, for 1 cm range of wave-lengths. (The last specification is responsible for the magnitudes in the table; for a working range of, say, 10A, it would be necessary to divide by 10^7.)

While a tungsten filament operated at a high temperature furnishes a convenient and widely used source of light for measurements in the visible

[1] "International Critical Tables," Vol. V, p. 238.

[2] Values are tabulated in the "International Critical Tables," Vol. V, p. 243, and by E. Lax and M. Pirani, *Handbuch der Physik*, Vol. XIX, p. 40 (Julius Springer, 1928).

spectrum, it will be seen from the table that the energy available in the ultra-violet is so small as to render such a source almost useless for measurements in this region. Some of the ultra-violet sources discussed in Sec. **12-19** are usually used. Since most of these sources furnish a

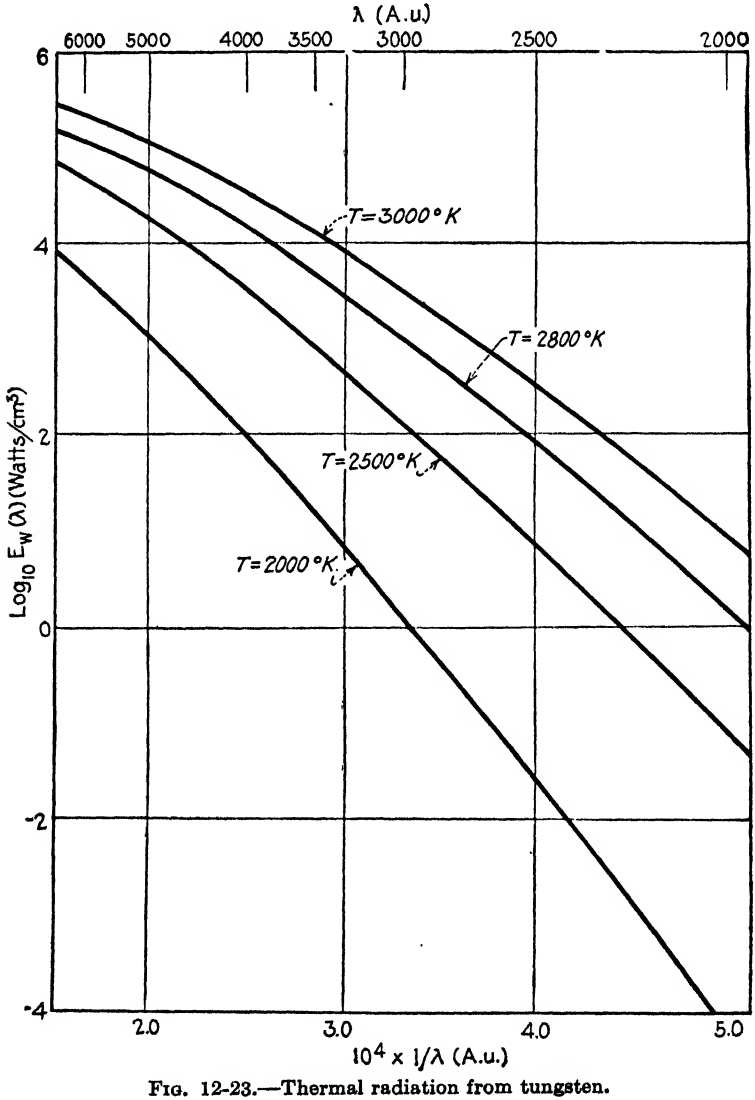


FIG. 12-23.—Thermal radiation from tungsten.

line spectrum it is necessary to determine experimentally the relative intensities of the various lines to be used. The only instrument suitable for this purpose at present is the thermopile, since it is the only one which yields a direct measurement of energy at any wave-length. The technique of thermopile measurements has been highly developed in recent

years, particularly in connection with studies of infra-red spectra. In most respects the same technique is applicable to the present problem.

The problem of the design and construction of sensitive thermopiles for radiation measurements is a considerable field in itself, and the reader must be referred to other sources[1] for detailed information. It may be worth while, however, to address a few remarks to those confronted with the problem of choosing, from the various types of thermopiles and galvanometers now on the market, the particular combination best suited to their needs.

The chief requirements to be met by sensitive radiation thermopiles are (1) high thermoelectric power, (2) low internal resistance, (3) small heat capacity, (4) low thermal conductivity. Obviously some of these requirements are conflicting, for an increase in thermoelectric power obtained by using many junctions in series may be nullified by the increased resistance. Any attempt to decrease the resistance will also result in an increased thermal conductivity. The particular compromise selected depends upon the type of measurements to be made and on the galvanometer available. For measurements of fairly intense spectral lines, a simple linear thermopile of 10 to 15 junctions is often used. The multiple-junction thermopile is to be preferred especially when the galvanometer to be used has an internal resistance of 50 ohms or higher. The sensitivity of such a thermopile as well as its stability may be considerably increased if it is mounted in vacuum. The Coblentz[2] instrument is of this type and is widely used in this country for spectral measurements.

Considerably greater sensitivity can be obtained, however, with the combination of a low-resistance galvanometer (*e.g.*, 15 ohms) with a single-junction vacuum thermopile of very small heat capacity.[3] Such thermopiles are now on the market,[4] the thermocouple wires being made exceptionally fine and the receiver consisting, in one type, of a small piece of thin, blackened gold foil, 1 or 2 mm^2 in area. It is necessary, of course, to focus the radiation (*i.e.*, an image of the monochromator slit) on to this receiver very carefully with a short-focus lens. Such thermopiles have a resistance of about 15 ohms.

The galvanometer to be used with a given thermopile must, of course, be carefully selected, since it is not high *current* sensitivity but high *voltage* sensitivity which is required. For this reason the resistance of the coil must be low; and to retain high sensitivity, exceptionally fine coil suspensions and intense magnetic fields are used.

[1] See especially T. Dreisch, *Handbuch der Physik*, Vol. XIX, p. 829, and H. Cartwright, *Rev. Sci. Instr.*, **1**, 592 (1930).

[2] W. W. Coblentz, *Jour. Opt. Soc. Amer.*, **5**, 356 (1921); *U. S. Bur. Standards, Sci. Papers* No. 413 (1921). The Coblentz vacuum thermopile is manufactured commercially by the Eppley Laboratories, Newport, R. I.

[3] W. Moll and H. C. Burger, *Zeits. f. Phys.*, **32**, 575 (1925); E. Pettit and S. B. Nicholson, *Astrophys. Jour.*, **56**, 295 (1922).

[4] The Moll thermopile is manufactured by Kipp and Zonen, Delft, Holland, and a modified form of the Pettit-Nicholson thermopile by R. C. Burt, Pasadena, Calif.

The development of low-resistance, high-sensitivity d'Arsonval galvanometers has rendered unnecessary, in most cases, the use of the troublesome moving-needle type of instrument formerly used. The best arrangement is obtained, of course, when the resistance of the thermopile and connections is just equal to the critical damping resistance of the galvanometer. In two galvanometers now on the market[1] the internal resistance is of the order of 15 ohms, the critical damping resistance is also 15 ohms, and the sensitivity of the order of 3×10^{-8} volt/mm.

The effective sensitivity of these galvanometers may be increased several times by increasing the scale distance, or several hundred times by magnifying the deflection by means of the Moll[2] thermo-relay or the Zernike[3] differential thermocouple. By means of these devices it has been found possible to bring the galvanometer sensitivity up to the theoretical limit set by Brownian motion fluctuations. As has already been pointed out,[4] it is impossible to amplify thermopile voltages directly by means of thermionic vacuum tubes, because the magnitude of the thermo-e.m.f. is nearly always far less than 1 microvolt, the smallest grid potential whose effect can be separated from shot-effect fluctuations in thermionic tubes.

In case it is necessary to know the actual amount of radiation emerging from the monochromatic illuminator in absolute units (*e.g.*, calories per second, ergs per second, or watts), it is necessary to calibrate the thermopile by determining the intensity of radiation falling on it which is required to produce a given deflection of the galvanometer. This can most easily be done by noting the galvanometer deflection when the receivers of the thermopile are allowed to intercept a known fraction of the radiation from a standard lamp whose power output is known. (For a vacuum tungsten lamp the power radiated is very nearly equal to that consumed, but this is not true for gas-filled lamps, due to losses by conduction.) The radiation may be allowed to fall on the thermopile directly, or, better, on a slit of known area behind which are placed the thermopile and a lens to focus an image of the slit on the receivers. In later measurements with the monochromator it is then necessary to make sure that all the energy emerging, or at least a *fixed* fraction of it, falls on the thermopile receivers. As an illustration of the magnitudes involved, it has been found that a single-junction vacuum thermopile of the type manufactured by R. C. Burt, when used with a Zernike-type Zc galvanometer, will give a deflection of 1 mm at a scale distance of 1 m when the radiation falling on the receiver has an intensity of about 3×10^{-10} cal/sec cm^2.

The relative intensities of the ultra-violet spectral lines in the light given out by a Cooper-Hewitt quartz mercury arc[5] (Uviarc), as trans-

[1] The Zernike galvanometer, type Zc, manufactured by Kipp and Zonen, and the Model 2285-X galvanometer of the Leeds and Northrup Company, Philadelphia.

[2] W. Moll and H. C. Burger, *Zeits. f. Phys.*, **34**, 109 (1925); see also catalogues of Kipp and Zonen.

[3] F. Zernike, *Zeits. f. Phys.*, **40**, 635 (1926).

[4] See Sec. **12-16**.

[5] Manufactured by the General Electric Vapor Lamp Company (formerly Cooper-Hewitt Electric Company).

mitted by a Hilger quartz monochromator, have been carefully measured by Kazda,[1] using a Pettit-Nicholson type of vacuum thermopile. Since this type of arc is widely used as an ultra-violet source, Kazda's values, together with some obtained by DuBridge, are tabulated in Table 12-7. Although the intensities of individual lines vary considerably with the operating conditions of the arc, the values given in the table should prove a useful guide. The operating conditions chosen by Kazda are those which give a brilliant arc of great steadiness. The intensities are given in arbitrary units, that of the line 2536A being taken as 1000. Correction has been made for the presence of continuous background radiation.

TABLE 12-7.—RELATIVE INTENSITIES OF HG SPECTRAL LINES*

λ A.u.	*I*	λ	*I*
2967	582.0	2345	20.0
2925	117.0	2302	10.6
2894	209.0	2284	13.6
2804	371.0	2253	6.60
2754	63.0	2225	7.90
2700	88.6	2191	4.75
2653	735.0	2150	2.74
2536	1000.0	1973	0.128
2482	218.0	1943	0.097
2399	51.5	1850	0.017
2378	40.0		

* As resolved by a Hilger quartz monochromator, using a Cooper-Hewitt 110-volt Uviarc operating at 92 volts, 2.1 amp.

[1] C. B. KAZDA, *Phys. Rev.*, **26**, 643 (1925).

CHAPTER XIII

APPLICATIONS OF THE PHOTOELECTRIC EFFECT

The past few years have witnessed an exceptionally rapid development in the technique of making sensitive photoelectric cells, and in the perfection of sensitive and reliable methods for detecting and measuring photoelectric currents. As a result, the number of uses which have been found for the photoelectric cell in the laboratory and in commercial devices has multiplied with bewildering rapidity. There is every evidence that in a short time the photoelectric cell will become nearly as well known and widely used as the thermionic vacuum tube. Commercial photoelectric cells of various types are now being manufactured in large quantities. The multiplication of their commercial uses has, in fact, provided the powerful incentive which is largely responsible for the development of the highly sensitive photoelectric cathodes described in the previous chapter.

A vast literature has grown up on this subject, and descriptions of newly developed applications are continually appearing in the various technical journals. At least three excellent books[1,2,3] have recently been published in English on the uses of photoelectric devices, and to these the reader is referred for a more complete account of the subject than can be undertaken here. The purpose of this chapter will be simply to call attention to some of the more important uses to which photoelectric cells have been put, paying particular attention to those of especial interest to the physicist.

The principal uses of the photoelectric cell in the laboratory have to do with the measurement and comparison of light intensities, and these are discussed in the first part of the chapter under the head of Photoelectric Photometry. The second part of the chapter will be devoted to a discussion of the rôle of the photoelectric cell in various commercial devices.

[1] N. R. Campbell and Dorothy Ritchie, "Photoelectric Cells" (Sir Isaac Pitman & Sons, 1929).

[2] V. K. Zworykin and E. D. Wilson, "Photocells and Their Application" (John Wiley & Sons, Inc., 1930).

[3] "Photoelectric Cells and Their Applications; a Discussion at a joint meeting of the Physical and Optical Societies," June, 1930. (The Physical and Optical Societies, London, 1930.)

PHOTOELECTRIC PHOTOMETRY[1]

13-1. General.—Because of the linear relation between photoelectric current and light intensity in properly designed cells, it was inevitable that one of the first, as well as one of the most widely used, applications of the photoelectric effect should be in the field of photometry. Photoelectric photometers of various types have now become so highly perfected that they are rapidly replacing visual and photographic methods, and in some cases the thermopile, in various types of light measurements.

There are a number of advantages of photoelectric over visual methods in photometry.[2] As it always is desirable whenever possible to substitute objective for subjective methods, so the replacement of visual observation by the measurement of a photoelectric current makes for greater speed and greater precision. The act of reading a meter is much simpler and capable of far greater precision than the visual matching of two illuminated fields. The photoelectric method also possesses the inherent advantage that it can be extended, if necessary, to measurements in the ultra-violet, or, with recently developed red-sensitive cells, in the infra-red portions of the spectrum.

There is a serious difficulty to be overcome, however, when the photoelectric cell is used to replace the human eye in determining the relative brightness[3] of two illuminations which are not of the same color. This is due to the fact that most photoelectric spectral distribution curves do not at all resemble the visibility curve of the eye, so that two illuminations of the same visual brightness might excite quite different photoelectric currents in a given cell. In fact the visual and photoelectric brightness will in general be the same, only if the energy distribution

[1] In the preparation of this section the authors have made considerable use of the material in Campbell and Ritchie, "Photoelectric Cells," and in the "Discussion on Photoelectric Cells." We are particularly indebted to the publishers of the "Discussion" for furnishing us with advance proof, and to Dr. K. S. Gibson, who furnished us with an advance copy of his manuscript and also communicated other information.

[2] See Campbell and Ritchie, "Photoelectric Cells," Chap. XIII (Sir Isaac Pitman, & Sons, 1929).

[3] Two illuminations are said to have the same visual brightness if they can be matched, as in an ordinary Bunsen photometer. They have the same "photoelectric brightness" if they give rise to equal photoelectric currents in a given cell. Strictly speaking, two illuminations can be "matched" visually, only if they are of the same color. But if the colors differ only slightly, as for example in two incandescent lamps operated at somewhat different temperatures, the eye is still able to judge approximate equality of brightness. The eye can even judge, with some practice, whether two illuminations of widely different color seem equally "bright," but in this case the concept loses quantitative significance.

There is never any difficulty about determining the relative photoelectric brightness of two illuminations, no matter what their color. But the ratio of the photoelectric currents produced by two given light beams may vary over wide limits, according to the type of photoelectric cell and filter used.

throughout the spectrum is the same for the two light sources, *i.e.*, if they have the same "color." Fortunately there are many practical problems in which this condition is sufficiently well satisfied (*e.g.*, the photometry of tungsten lamps operating at a fixed temperature). But in other cases it is necessary to employ filters in connection with the photoelectric cell so that the response curve of the cell plus filter will more nearly resemble the visibility curve of the eye. If they are the same, then two illuminations of the same visual brightness will give rise also to the same photoelectric currents. The filters which are required to bring about this condition are usually those which absorb the blue and violet portions of the spectrum to which the photoelectric cell is very sensitive and the eye quite insensitive. In Fig. 13-1, curve *A* represents the visibility curve of the average human eye; curve *B* is the spectral distribution curve for a caesium photoelectric cell used without filter; and curve *C* is the resultant distribution curve when the same cell is used in conjunction with a Wratten K-3 filter.[1] Curves *A* and *C* do not accurately fit, but they are sufficiently close for most photometric work.

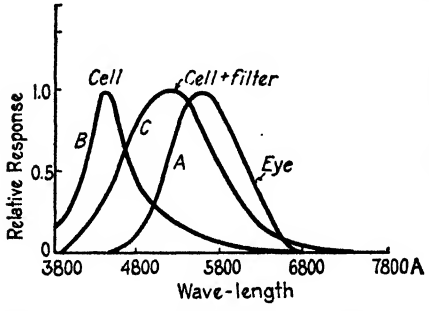


FIG. 13-1.—*A*. Visibility curve for average human eye. *B*. Spectral distribution curve for caesium photoelectric cell. *C*. Distribution curve for same cell with filter K-3.

13-2. Methods of Measurement.—Photoelectric photometers may make use of any of the methods for measuring photoelectric currents which were described in the previous chapter. The method to be chosen will depend upon the particular type of photometric measurements to be made, upon the precision required, the type of photoelectric cells available, as well as upon other requirements such as simplicity of operation, ruggedness and reliability, etc. We review briefly, for reference, the requirements of the three general methods of measurement which were previously discussed.

1. *Direct Method.*—The light intensities are compared directly in terms of the photoelectric currents produced in a given cell. To obtain quantitative results it is necessary (*a*) that the cell have a linear response, (*b*) that its sensitivity does not change appreciably with time, and (*c*) that a constant standard source of light be available. This method is the simplest of all and can be made to yield excellent results with well-constructed cells and proper standards.

[1] Taken from C. Deshler and H. Schroeder, *Trans. Amer. Illum. Eng. Soc.*, **23**, 391 (1927).

2. *Balanced Cell Method.*—In this case two photoelectric cells are used, one illuminated by the test and the other by the standard illumination. If these are derived from the same initial source of light, variations in the source will cancel out, since only the difference in the two photoelectric currents is measured. It is not necessary that the cells be identical in sensitivity but they must not change with time, or at least they must change at the same rate. As Campbell and Ritchie[1] have pointed out, this method is not as satisfactory nor as widely used as the two others.

3. *Equal Deflection Method.*—In this case a single cell is used, illuminated alternately by the test and the standard beam of light. It is necessary that the standard be continuously variable in known ratios[2] and its intensity is then adjusted until the photoelectric currents produced by the two beams are the same. With this method it is not necessary that the cell be linear, and it may even vary with time. Even rapid variations in the cell with time, or rapid variations in the source, may be canceled out if the change, from standard to test beam and back, be made at high frequency, *e.g.* 25 times per second, and if the two beams are derived from the same light source. When some scheme is used for rapidly alternating the two light beams falling on the cell this method of comparing light intensities is conveniently referred to as the "flicker" method. In this case the balance is obtained by adjusting the intensity of one light beam until there is no alternating component to the photoelectric current. Extremely high precision has been obtained in photometers making use of some form of the equal-deflection method.

The instruments used for current measurements in any of these photoelectric methods depend of course upon the sensitivity desired, and on the intensity of the light sources available. Galvanometers and electrometers are generally used in experimental work in laboratories, but, in commercial photometers or in laboratories where routine photometric measurements are made, amplification methods of various kinds have come into wide use.

13-3. Photometry of Lamps.—This is an important field in which photoelectric methods are finding a wide application. Some form of the "direct" method of measurement is usually employed for the sake of simplicity. Such methods have been found in actual practice to yield results consistent to 0.5 per cent. In routine visual measurements, on the other hand, the errors are seldom less than 1, and often as high as 4 per cent.[3]

Several very conveniently arranged forms of photoelectric photometers for lamp calibration, which are now in everyday use in lamp

[1] CAMPBELL and RITCHIE, "Photoelectric Cells," p. 170.

[2] For methods of accomplishing this, see Sec. **12-17**.

[3] G. T. WINCH, *Jour. Inst. Elec. Eng.* (*London*), **68**, 553 (1930).

development and testing laboratories, have recently been described.[1,2,3] All make use of essentially the same method (Fig. 13-2). The lamp under test is placed at the center of a white integrating sphere, or box, of the type commonly used in visual photometry. The light emerging from a small opening falls either directly or after diffusion by opal glass or by another smaller sphere[4] onto a photoelectric cell. The current from the cell is fed into a bridge amplifier of the type shown in Fig. 12-18, page 448. The null method is used, the galvanometer deflection being brought to zero by means of the variable grid bias. The apparatus is calibrated by means of standard lamps, usually in such a way that the potential divider supplying the grid bias, or the voltmeter which measures it, will read the output of the lamp directly in lumens.[5]

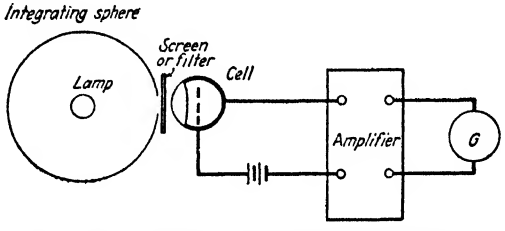


FIG. 13-2.—Simple photoelectric photometer.

When the lamps to be compared are all operating at the same temperature, no filter is required. Otherwise a suitable filter may be placed in position to intercept part of the light falling on the cell, and its exact position adjusted until the same reading is obtained for two lamps which have the same visual intensity but are operated at different temperatures.

The cells used are either of the potassium hydride or of the newer Cs-CsO-Ag type which have the greatest sensitivity to white light. The vacuum-type cells are preferred where great constancy is desired, but gas-filled cells operated at low magnification are often used.[6]

The most highly developed form of the flicker method of measurement applied to the photoelectric photometry of lamps has been described by Sharp and Smith.[7] Their arrangement is shown in Fig. 13-3. The

[1] G. T. Winch, *Jour. Inst. Elec. Eng.* (*London*), **68**, 553 (1930).

[2] C. H. SHARP and H. A. SMITH, *Trans. Amer. Illum. Eng. Soc.*, **23**, 429 (1927); "Discussion on Photoelectric Cells," p. 110.

[3] C. DESHLER and H. SCHROEDER, *loc. cit.*

[4] See CAMPBELL and RITCHIE, "Photoelectric Cells," p. 169.

[5] A summary of the illumination units used in photometry will be found in the Appendix.

[6] See also papers by the Research Staff of the General Electric Company (London), *Jour. Sci. Instr.*, **3**, 2, 38, and 77 (1925); E. A. BAKER, *Jour. Sci. Inst.*, **1**, 345 (1924); J. O. PERRINE, *Phys. Rev.*, **22**, 48 (1923); T. H. HARRISON, "Discussion on Photoelectric Cells," p. 118.

[7] C. H. SHARP and H. A. SMITH, *loc. cit.* See also G. M. B. DOBSON and D. S. [illegible], "Discussion on Photoelectric Cells," p. 79.

rotating mirror consists of a disk of glass, one half of which is silvered and the other half clear. During half of each revolution light from the comparison lamp falls on the cell while during the other half light is received from the test lamp. The output of the photoelectric cell is amplified by a resistance-capacity coupled amplifier and then, by means of the contactor which is operated on the shaft that rotates the mirror, is rectified, and finally measured with a galvanometer. The rectification is so arranged that when the test lamp is stronger the galvanometer deflects in one direction, and in the opposite direction, when the comparison lamp is the stronger. Adjustment is then made for zero deflection by moving the comparison lamp along an optical bench.

As an example of the great saving of time which can be effected through the use of photoelectric methods in routine lamp photometry,

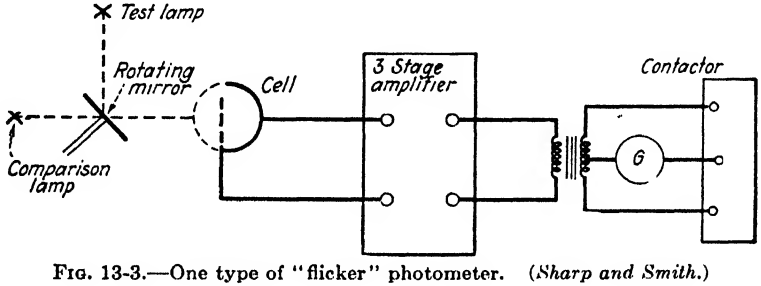


FIG. 13-3.—One type of "flicker" photometer. (*Sharp and Smith.*)

Winch[1] records that a series of measurements which, by visual methods, occupied the time of five observers at intervals over a period of 4 days, were repeated with far less fatigue and greater precision by a single observer, using the photoelectric method, in a period of 4 hr.

13-4. Photoelectric Microphotometers.—The measurement and recording of densities of spectrum lines on photographic plates are usually accomplished by focusing the light transmitted by a limited region of the plate on to a thermopile or a photoelectric cell. The advantages and disadvantages of one over the other seem to be about equally divided.[2] The photoelectric cell yields larger currents, but the thermopile is probably more reliable. However, when it comes to amplification, the photoelectric cell has a distinct advantage and hence may be expected gradually to replace the thermopile in such instruments. This advantage is due to the fact that the photocell gives, for a fixed illumination, a definite *current*, nearly independent of the external resistance. The thermopile gives a definite *voltage*, the current depending on the circuit resistance. Now the smallest *potential* which can be successfully amplified by a thermionic tube is definitely limited to the order of about 1 microvolt by the unavoidable shot-effect fluctuations in the thermionic

[1] G. T. WINCH, *Jour. Inst. Elec. Eng.* (*London*), **68**, 553 (1930).
[2] F. GOOS and P. P. KOCH, *Phys. Zeits.*, **27**, 41 (1926).

current.[1] On the other hand, *any current*, however small, may be amplified, provided only that it is passed through a resistance high enough so that the potential drop across it, due to the current, be greater than 1 microvolt. Hence, with a photoelectric cell and amplifier, a much sturdier and more stable measuring and recording instrument may be employed than is possible with a thermopile.

The direct-deflection method, with one stage of amplification, may be conveniently employed, and the galvanometer deflections recorded photographically. It is important that a galvanometer of very short

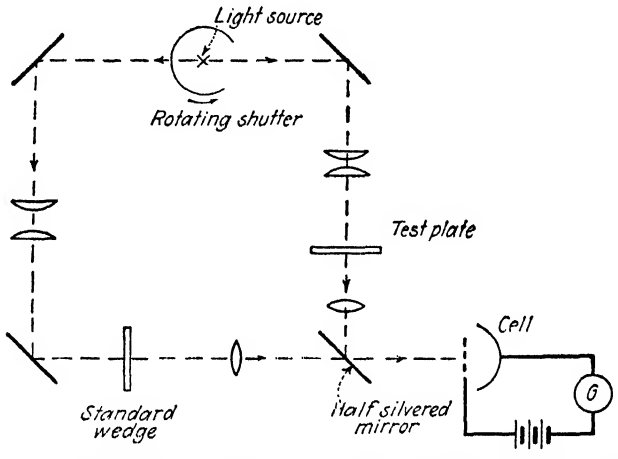


FIG. 13-4.—Photoelectric microphotometer using "flicker" method. (*Dobson.*)

period, such as a Moll microgalvanometer, be used so that the record for a given plate may be made in as short a time as possible. Variations in the cell sensitivity and light intensity will then be of less consequence. Such an instrument is now in use in the Physics Laboratories at Washington University, and is giving satisfactory results. The new FP-54 amplifying tubes are used.

For greater precision the flicker method has been employed by Dobson,[2] using the arrangement shown in Fig. 13-4. Two beams of light are taken alternately from the same source by means of a rotating shutter. One passes through the test plate to the photoelectric cell, the other passing through a calibrated wedge. The latter is adjusted until fluctuations of the photocurrent cease. The method is capable of a precision of 0.1 per cent, according to the author, but has the disadvantage that automatic recording cannot be employed without considerable elaboration.

[1] A. W. HULL and N. H. WILLIAMS, *Phys. Rev.*, **25**, 147 (1925).
[2] G. M. B. DOBSON, *Proc. Roy. Soc.*, **104**, 248 (1923).

Goos and Koch[1] have made use of the balanced-cell method shown in Fig. 13-5. A record is made of the deflection of the string galvanometer which reads the difference between two photocurrents, one due to the direct and the other to the transmitted beam. Variations in the light source thus cancel out, though variations in an individual cell do not. The arrangement described by Goos and Koch has been made the basis for an elaborate commercial form of microphotometer, manufactured by A. Krüss, Hamburg.[2]

13-5. Spectrophotometry.[3]—As has already been pointed out, the photoelectric cell is particularly adapted to the measurement of the relative intensities of two illuminations of the same wave-length or color.

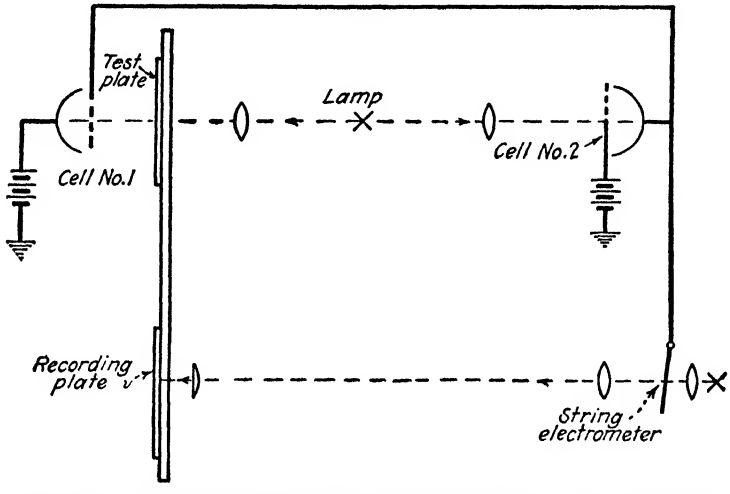


FIG. 13-5.—Balanced-cell recording microphotometer. (*Goos and Koch.*)

For such measurements there is no question as to the spectral distribution of sensitivity ("color sensitivity") of the particular cell used, and an absolute comparison of intensities is possible. As a result, photoelectric methods have come into wide use in the field of spectrophotometry during the past few years, particularly in instruments designed for the

[1] F. Goos and P. P. Koch, *Zeits. f. Phys.*, **44**, 855 (1927); P. P. Koch, *Ann. d. Phys.*, **39**, 705 (1912); "Discussion on Photoelectric Cells," p. 150; also H. Rosenberg, *Zeits. f. Instr.*, **45**, 313 (1925); P. Lambert and C. Chalonge, *Rev. d'Opt.*, **5**, 404 (1926); F. C. Toy, *Jour. Sci. Instr.*, **4**, 369 (1927).

[2] Since this section was written, the following paper has appeared: "Microphotometric Measurements" by E. G. Jones and H. L. Brose (*Jour. Sci. Instr.* **8**, 145 [1931]).

[3] In the preparation of this section the authors have made extensive use of the excellent critical review of this subject given by K. S. Gibson in his article in "Discussion on Photoelectric Cells." See also the report of the Committee on Spectrophotometry (K. S. Gibson, chairman), *Jour. Opt. Soc. Amer.*, **5**, 527 (1922).

measurement of the transmission or reflecting power of materials throughout the spectrum (*i.e.*, color analyzers). Such instruments are of use, not only in the scientific laboratory (for studies of absorption spectra, analysis of dyes and other organic compounds, light filters, etc.), but also in industry where color has come to have a distinct commercial importance.

As Gibson[1] has pointed out, it is in the field of spectrophotometry that visual methods are also at their best, so that "a good observer with a good instrument can, by averaging five or ten observations at each wave-length, readily obtain a mean result whose probable error is but a fraction of 1 per cent." The increase in *accuracy* made possible by photoelectric methods is not therefore of great importance. However, they do allow a very great increase in the *speed* of determination. This increase in speed is "the outstanding feature of importance in photoelectric spectrophotometers."[1] It is made possible partly by the fact that photoelectric measurements are more *reproducible* than visual measurements, so that only a single measurement at each wave-length is necessary. In addition, the photoelectric currents can be used for automatic recording or control. The making of photoelectric measurements requires less skill on the part of the observer, and also gives rise to less fatigue; but the skill and care required in the design of an accurate photometer are the same regardless of the method of detection.

It is not surprising that the first applications of photoelectric methods to spectrophotometry were in the ultra-violet portions of the spectrum, which had hitherto been almost inaccessible by other methods. A number of observers studied the absorption of gases by this method;[2] Winther determined the extinction coefficient of fluorescent solutions;[3] Hulbert[4] and Frehafer[5] made measurements on the specular reflecting power of metals in the ultra-violet. The method used in each case was the direct method, in which measurements were made of the photoelectric current excited (1) by the incident beam, and (2) by the reflected (or transmitted) beam. The ratio of (2) to (1) gave directly the "reflectance"[6] (or transmission) of the substance under test. Monochromatic light was furnished by resolution through quartz prisms, and alkali-metal cells were usually used with quartz or fluorite windows. Electrometers were used to measure the currents. This direct method is quite reliable if properly designed cells are employed and because of its great simplicity has found a wide application in laboratory measurements throughout

[1] K. S. Gibson, *loc. cit.*, p. 160.
[2] See H. von Halban, *Zeits. f. Phys. Chem.*, **96**, 214 (1920).
[3] C. Winther, *Zeits. f. Elektrochem.*, **19**, 389 (1913).
[4] E. O. Hulbert, *Astrophys. Jour.*, **44**, 137 (1916).
[5] M. K. Frehafer, *Phys. Rev.*, **15**, 110 (1920).
[6] "Reflectance" = monochromatic reflecting power.

the ultra-violet spectrum (*i.e.*, from 1850A to 4000A). During the past few years the method has been extensively used to replace visual measurements in the visible spectrum, and has been applied to such problems as the measurement of the reflecting power of alkali metals,[1] the absorption of solutions,[2] and many others too numerous to mention.

A balanced-cell method of measurement developed by Gibson[3] was used for many years by the U. S. Bureau of Standards in making color analyses of colored glasses, of dye solutions, and of colored papers (Fig. 13-6). "For the spectral transmission measurements, the amount

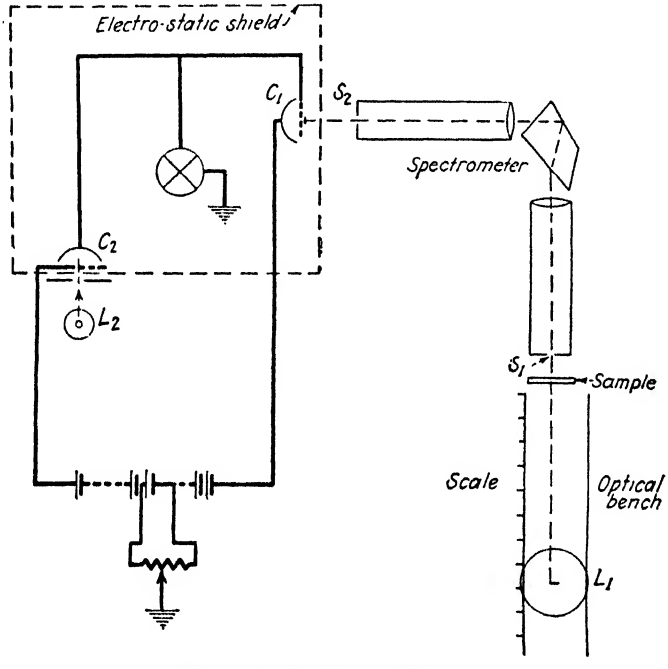


FIG. 13-6.—Balanced-cell spectrophotometer. (*Gibson.*) L_1, 600-watt lamp. L_2, 14-watt lamp. S_1, S_2, spectrometer slits.

of energy entering the spectrometer slit was varied by varying the distance from the source to the slit. The photoelectric current thus produced was balanced by the photoelectric current of the second cell irradiated by a small lamp. The two lamps were operated in parallel, with suitable resistances, on a storage battery. The transmission sample was then inserted before the spectrometer slit and the balance restored

[1] J. B. NATHANSON, *Astrophys. Jour.*, **44**, 137 (1916).

[2] H. VON HALBAN and H. GEIGEL, *Zeits. f. Phys. Chem.*, **96**, 214 (1920); H. VON HALBAN, *Proc. Roy. Soc.*, **116**, 153 (1927).

[3] K. S. GIBSON, *U. S. Bur. Standards Sci. Papers* 349, October, 1919. See also *Papers* 148, 167, and 440.

by moving the lamp toward the slit by the necessary amount. The transmission was then computed from the inverse square of the distances. Rotating sectors were used to extend the range of the measurements."[1] In the diffuse reflection measurements the intensity of the light reflected from the sample was compared with the intensity of the same beam reflected from a standard "white" surface ($MgCO_3$ or MgO). A similar method was developed by von Halban and Siedentopf[2] for measurements of the light absorption of solutions, except that the intensity variations were made with a rotating sector.[3]

In 1923 Gibson[4] developed a photoelectric spectrophotometer, designed for transmission measurements, which excelled in speed and precision the one described above. This instrument is quite similar to that shown in Fig. 13-6 except that an equal deflection method was used with a galvanometer and single cell. "The sample and a Brodhun rotating sector[3] are placed between two lenses used to focus the image of a gas-filled lamp filament on the spectrometer slit. With the Brodhun sector at 100 the galvanometer reading is noted; the sample is then removed from the beam and the sector adjusted to give the same galvanometer reading as before. This sector reading is taken as the transmission of the sample."[1]

In recent years a number of photoelectric photometers have been designed, based for the most part on the principles outlined above, in which amplification of the photoelectric current is employed in order to allow the measurements to be taken with a more rugged galvanometer or microammeter, or, in some cases, to make possible automatic recording.[5] The best example of these is probably the very ingenious color analyzer described by Hardy,[6] shown in Fig. 13-7. The test surface and a standard surface of $MgCO_3$ are illuminated by two beams of light from the same ribbon-filament tungsten lamp. The two reflected beams are admitted alternately, by a rapidly rotating sectored mirror, to the slit of a spectrometer and then to the photoelectric cell. When the two beams are of unequal intensity there will be a pulsating current in the photoelectric cell circuit. "This current is amplified and the alternating component is applied to the field coils of a small motor, the armature

[1] Quoted from Gibson, "Discussion on Photoelectric Cells," p. 166.

[2] H. von Halban and K. Siedentopf, *Zeits. f. Phys. Chem.*, **100**, 208 (1922).

[3] For a discussion of the use of rotating sectors see Sec. **12-17**, p. 450.

[4] K. S. Gibson, *Jour. Opt. Soc. Amer.*, **7**, 693 (1923).

[5] See, for example, C. H. Sharp, *Jour. Opt. Soc. Amer.*, **13**, 304 (1926); *Trans. Amer. Illum. Eng. Soc.*, **23**, 419 (1928); "Discussion on Photoelectric Cells," p. 110; L. H. Tardy, *Rev. d'Opt.*, **7**, 189 (1928); A. H. Taylor, *Jour. Franklin Inst.*, **206**, 241 (1928); D. S. Perfect, "Discussion on Photoelectric Cells," p. 174. See also bulletins of the American Photoelectric Corporation, New York.

[6] A. C. Hardy, *Jour. Opt. Soc. Amer.*, **18**, 96 (1929).

being supplied from an independent source of the same frequency. With this arrangement the armature rotates in one direction when the beam from the specimen is more intense, and in the opposite direction when the beam from the standard source is more intense. When the intensities are equal the motor stops. By causing the motor to control a diaphragm which varies the illumination on the magnesium carbonate, the intensities of the two beams are automatically balanced. A pen operating on a rotating drum records the position of this diaphragm while the rotation of the drum changes the wave-length and width of the spectral band admitted to the photoelectric cell. In this way a complete spectrophotometric curve for the entire visible spectrum is traced in approximately thirty seconds."

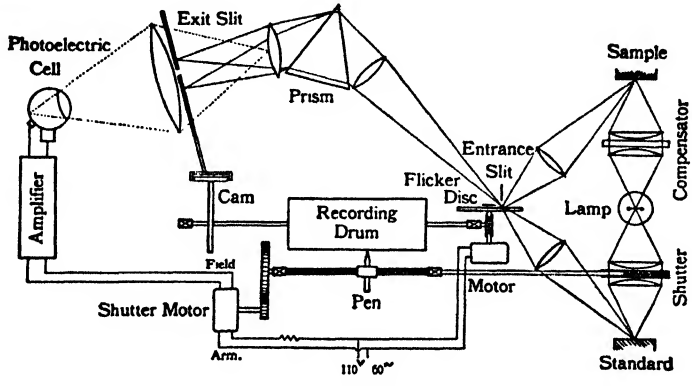


FIG. 13-7.—Recording photoelectric color analyzer. (*Hardy*.)

A modified form of the Hardy color analyzer is now being produced commercially by the General Electric Company. Some changes in the optical system have been made so that the dispersion of the light takes place before reflection from the specimen and standard surfaces. In place of the last stages of power amplification by ordinary tubes, a thyratron is used, making for considerable simplification in the amplifier circuit (see Sec. **13-7**, page 483).

A recording spectrophotometer for transmission measurements has been described by Müller,[1] who makes use of a method of interpolation. The photoelectric currents are measured by a string galvanometer whose deflections are recorded photographically. At each wave-length a record is made (1) of the deflection due to the beam transmitted by the sample under test, and (2) of the deflections obtained when, in turn, 0, 20, 40, 60, 80, and 100 per cent of the incident beam is cut out by a rotating sector. As different wave-lengths are brought to the slit by rotation of the prism, the photographic plate is automatically shifted so

[1] C. MÜLLER, *Zeits. f. Phys.*, **34**, 824 (1925).

that a complete transmission curve is plotted, together with a series of reference points which serve to calibrate the record.

The photoelectric measurement of intensities of ultra-violet radiation finds an important application in the biological sciences where considerable work has been done on the effects of ultra-violet light on plant and animal life.[1] In such problems the thing of interest is not usually the intensity of radiation in a single wave-length, but the total intensity of light from a given source which is within a certain wave-length region. The wave-length region most effective biologically lies, generally speaking, between the wave-lengths 2500A and 3100A. Measurement of the intensity of radiation in this region can be made directly with a photoelectric cell combined with a suitable filter. Since cadmium has a photoelectric threshold in the neighborhood of 3100A, cadmium cells have been widely used in this field. When mounted in bulbs of Uviol glass they are sensitive only to the band between 2600A and 3100A. Alkali-metal cells are not well suited for such measurements, since it is difficult to find filters which are transparent to the ultra-violet and opaque to the visible. It is therefore customary to choose a metal whose threshold is near the long wave-length limit of the region to be studied, and to use filters to eliminate the shorter wave-lengths. Such cell-filter combinations can be used, for example, to measure directly the changes in the ultra-violet content of sunlight. Measurements of this type are of particular value for "dosage" determinations in phototherapy.[2]

In connection with this discussion of spectrophotometry, it may be well to call attention to a very fertile but as yet almost wholly undeveloped field of usefulness for the photoelectric cell, namely, the measurement of the relative intensities of lines in the visible and ultra-violet spectra of light sources. This problem is one of steadily increasing theoretical and practical interest to physicists. At present the thermopile is most widely used for measurements of this type. While this instrument is admirably suited for measurements in the infra-red, it is well known that the energy associated even with the strongest lines in the ultra-violet spectrum of, say, a mercury arc, is so small that it can be detected only by thermopile-galvanometer systems of the very highest sensitivity. For the weaker ultra-violet lines the thermopile is useless. Photographic methods have found some use in the visible

[1] For a discussion of this subject and a list of references, see the articles by H. D. Griffith and by V. E. Shelford in "Discussion on Photoelectric Cells," also Campbell and Ritchie, "Photoelectric Cells," p. 180.

[2] The following papers describe other applications of the use of photoelectric spectrophotometers: H. von Halban and E. Zimpelmann, *Zeits. f. Elektrochem.*, **34**, 387 (1928) (use in microanalysis); H. A. Copaux, *Comptes Rend.*, **181**, 1058 (1925) (transmission of colored glass); J. Orcel, *Comptes Rend.*, **185**, 1141 (1927) (measurement of reflectivity); see also Sec. **13-12**.

but they are cumbersome, at best. The photoelectric method at once suggests itself. For while the small *voltages* (*e.g.*, 10^{-8} volt) furnished by a thermopile can be measured only with great difficulty, it is not difficult to measure (or to amplify) *currents* as small as 10^{-16} amp. Since in this case it is desired to compare the intensity of light at different wavelengths, it is necessary to obtain first the spectral distribution curve of the cell used. (A pure sodium cell in a quartz bulb has been found quite suitable.) This could be done by measuring the response of the cell to a number of the strongest lines in the spectrum of an intense source, the relative intensities of these lines being first determined with a thermopile. If a cell with a linear characteristic had been chosen, it would thus be calibrated and hence admirably suited for measurements of very feeble spectral lines. An alternative method would be to calibrate the cell against a source whose energy distribution is known, *e.g.*, a tungsten filament.

An investigation of the possibilities of this method is now under way at Washington University, and the authors are aware that other investigations of the same type are in progress elsewhere.[1] It is believed that a further study of this question will place in the hands of experimental physicists a powerful tool which will be of value in many research problems.[2]

13-6. Stellar Photometry.—The use of photoelectric cells for the measurement of the intensities of star images was reported at least as early as 1913, and attempts to use selenium cells had been made still earlier.[3] Accounts of the methods now in use have been given principally by Stebbins,[4] Guthnick,[5] H. Rosenberg,[6] and others.[7]

The chief problem to which photoelectric methods have been applied in astronomy is that of measuring light variations of variable stars.[8] In

[1] See CAMPBELL and RITCHIE, "Photoelectric Cells," p. 177.

[2] Since this section was written, the following papers on matters connected with it have appeared: "Photoelectric Cells in Colorimetry" by H. E. Ives and E. F. Kingsbury (*Jour. Opt. Soc. Amer.*, **21**, 541 [1931]); "Spectrophotometry" by K. S. Gibson (*Jour. Opt. Soc. Amer.*, **21**, 564 [1931]); "Some Comparative Spectrophotometric Measurements" by M. Barnard and P. McMichael (*Jour. Opt. Soc. Amer.*, **21**, 588 [1931]); "A Photoelectric Spectrophotometer for Measuring the Amount of Atmospheric Ozone" by G. M. B. Dobson (*Proc. Phys. Soc. Lond.*, **43**, 324 [1931]).

[3] See W. F. SCHULZ, *Astrophys. Jour.*, **38**, 187 (1913); P. GUTHNICK, *Astron. Nachr.*, **196**, 357 (1913); *Ber. Astron. Ges.*, **48**, 210 (1913).

[4] J. STEBBINS, *Publications of the Washburn Observatory* (1928).

[5] P. GUTHNICK, *Zeits. f. Instr.*, **44**, 303 (1924).

[6] H. ROSENBERG, *Naturwiss.*, **9**, 359 (1921).

[7] A. F. LINDEMANN and F. A. LINDEMANN, *Roy. Astron. Soc.*, **86**, 600 (1926); W. U. SMART, *Roy. Astron. Soc.*, **89**, 545 (1929); E. BOUTY, *Rev. d'Opt.*, **5**, 31 (1926); E. E. CUMMINGS, *Lick Observatory Bull.*, p. 99 (1923).

[8] We understand that experiments are now in progress at the Mount Wilson Observatory to investigate the possibility of using sensitive cells and amplification

such measurements, photoelectric methods have two important advantages over photographic. In the first place, they are capable of greater precision than is possible in visual and photographic methods. In the second place, they may be more easily adapted to obtaining a continuous record of brightness, and thus detecting variations of very short period. According to Stebbins,[1] the faintest stars which can be accurately measured (using a 16-in. telescope) are of the seventh magnitude, though the light from fainter stars can be detected. The photoelectric current obtained for stars of the seventh magnitude were, with the sensitized potassium cell in quartz used by Stebbins, of the order of 10^{-13} amp.

Stellar photometry presents a number of difficulties not met with in other types of photoelectric work. One of the chief of these is the exceedingly small light intensities available. This makes it necessary to make use of every available method of increasing the sensitivity of the photoelectric cell. Sensitization by a glow discharge and gas filling are always used. Potassium cells of the type described by Kunz and Stebbins[2] are usually employed, often in quartz for better insulation. The new commercial Cs-CsO-Ag cells are more sensitive, but usually not sufficiently well insulated for measuring very small currents. There seems to be room for progress in adapting these highly sensitive cells to work of this kind.[3]

The smallness of the photoelectric currents, however, would not be so serious an obstacle, were it not also necessary to impose severe requirements on the measuring instruments due to the wide variations in temperature, humidity, and other physical conditions in the observatory. These demand elaborate precautions to prevent insulation leaks. Fortunately, the photoelectric currents themselves are not sensitive to temperature changes, although temperature effects, due to changes in the gas pressure, are sometimes observed. Finally, to eliminate insulation troubles and large electrostatic capacity of long lead wires, it is necessary that the measuring instrument be mounted directly on the telescope. This means that it must be of exceptionally rugged construction, and instruments such as the Compton electrometer are at once eliminated. The Lindemann electrometer (see Sec. **12-10**) was particularly designed to fulfill these requirements, and is often used. Stebbins has had considerable success with a string electrometer. In either case, however, it is difficult to attain a sensitivity as great as 10^{-15} amp per scale division, so that accurate measurements cannot be obtained for currents much smaller than 10^{-13} amp.

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methods for the direct measurement of intensities of lines in solar and possibly stellar spectra.

[1] J. Stebbins, *Publ. Washb. Obs.* (1928).

[2] J. Kunz and J. Stebbins, *Phys. Rev.*, **7**, 62 (1916).

[3] See however footnote 2 on page 424.

Amplification methods would seem to offer the best solution to the problem, and they have been used with success by Rosenberg[1] and others. It is believed, however, that with the new FP-54 tubes now available (see Sec. **12-16**) the measurements can be extended to currents 100 times smaller than the present limit. This would make possible, with the photoelectric cells now in use, the accurate photometry of stars of the twelfth magnitude.

The method of taking the light curve for a variable star is usually the straightforward one of measuring the photoelectric current as a function of time, making use of a cell with a linear characteristic, or one which has been carefully calibrated. In order to eliminate slow changes in cell sensitivity and, of still more importance, variations in atmospheric absorption, it is necessary that measurements on the star under test be alternated with observations on a comparison star of known constancy and, preferably, of about the same brightness and color. Obviously the two stars must be close together in the sky, so that the telescope may be shifted from one to the other without too great inconvenience or loss of time. The use of photoelectric methods in this field has led to the discovery of many interesting phenomena and has revealed the existence of variable stars of very short periods which could not be studied in any other way.

Photoelectric cells in conjunction with filters have also been used in the study of the color index of stars. They may also be used to record accurately the time of passage of a star across the meridian and so be used as an accurate regulator of astronomical clocks.[2]

13-7. Photoelectric Relays.—By means of relays of various sorts, it is possible to make the minute currents furnished by a photoelectric cell control much larger currents, which in turn may be made to operate many kinds of electrical or mechanical devices. This offers a fertile field for the so-called practical applications of photoelectric cells; in fact the number of such devices which have been or can be devised seems to be almost without limit.[3]

Photocurrents may be called upon either to start or stop a process, or to give continuous control. In the first case all that is required is an ordinary relay which is either "on" or "off," according to whether the exciting current is above or below a certain critical value. Usually the photocurrent itself is too small to operate any but the most sensitive

[1] H. Rosenberg, *Naturwiss.*, **9**, 359 (1921).

[2] Since this section was written this paper has appeared: "The Alt Photoelectric Spectralactinometer" by H. Goldschmidt and R. Fleischer (*Zeits. f. Instr.*, **51**, 417 [1931]).

[3] Many such applications are described in various articles in *Electronics* (1930–1931).

relays of the mechanical type, and hence must first be amplified.[1] Two or three relays in series are used where large amounts of power are to be controlled. Obviously the output current of the relay may be used for a variety of purposes: to start or stop a motor which is performing some function, to turn lights on or off, to give an alarm, etc. Anything which produces a change in light intensity falling on the cell may be made to operate the relay. Objects may be counted by their shadows falling on a cell; signal or display lights may be turned on or off according as the daylight illumination falls below, or rises above, a certain value; objects may be sorted or registered according to size, color, transparency, etc.; a slitted clock pendulum may allow a flash of light to pass once each second and this can be transformed into an audible time signal, or used for the regulation of "slave" clocks by a single "master."

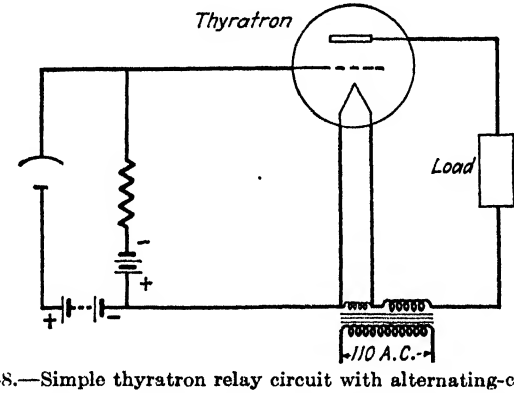

FIG. 13-8.—Simple thyratron relay circuit with alternating-current control.

Mechanical relays, even of the best type, have several disadvantages which seriously restrict their use. Usually they cannot be operated by the photoelectric current directly, so that an initial stage of amplification is required. The electrical contacts, after repeated operations, deteriorate and give trouble. They may not operate instantaneously, and hence introduce an undesirable time lag. Finally, the threshold value of the current at which the relay is supposed to operate is not sharply defined and is different for the "on" and the "off" operation, so that a sort of "hysteresis" is observed. In spite of their disadvantages, however, mechanical relays of the better type are of wide usefulness, and there are many problems in which their shortcomings are not of importance.

Quite recently a new type of thermionic tube has become available which is admirably adapted for use as a relay in conjunction with a photoelectric cell, and in which all of the above objections are eliminated. These tubes, known under the trade names of "thyratron" or "grid-glow

[1] However the new rectifier photo-cells (developed by Lange and by the Weston Electrical Instrument Corp.) yield currents large enough to operate sensitive relays directly.

tube"[1] promise to find a wide application in photoelectric-cell circuits, in addition to other uses. A brief description of them may not be out of place.

The thyratron[2] is essentially a hot-cathode, mercury-arc rectifier in which a control grid has been placed between cathode and anode. The cathode is of special construction, being heat insulated and of large emitting area, so that even when operated at low power it is capable of furnishing thermionic currents of many amperes! With the anode at a definite positive potential with respect to the cathode, no current will pass until the grid potential is raised above a certain critical value, usually slightly negative. When the grid potential is raised to this value, an arc suddenly starts and the full current flows, limited only by the electron emission of the cathode and the resistance in the anode circuit. Once the arc starts, however, the grid loses control (due to the sheath of positive ions formed around it) and no longer has any effect on the discharge, regardless of its potential. The arc may be stopped only by removing the anode potential.

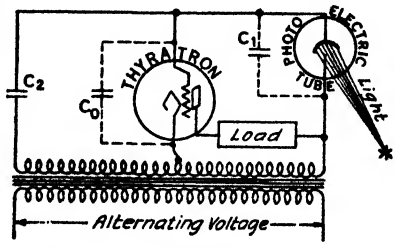

FIG. 13-9.—Thyratron circuit with phase control by a photoelectric cell. (*Hull.*)

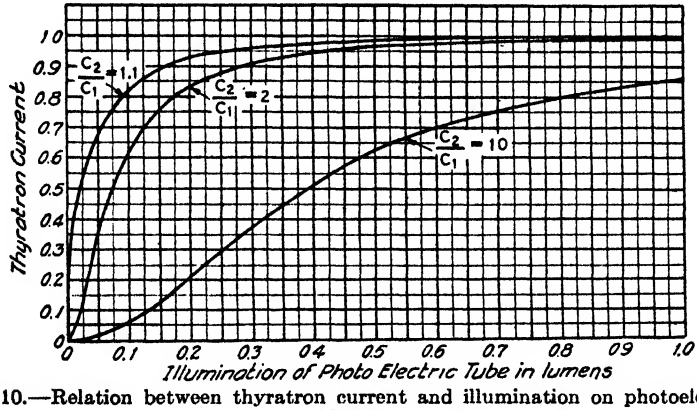

FIG. 13-10.—Relation between thyratron current and illumination on photoelectric cell for circuit of Fig. 13-9. (*Hull.*)

The grid may be used to stop, as well as to start, the current by the simple expedient of applying an alternating voltage to the anode. The arc

[1] Manufactured by the General Electric Company and the Westinghouse Electric and Manufacturing Company, respectively.

[2] See A. W. HULL, *Gen. Elec. Rev.*, **32**, 213 and 390 (1929), for a more complete account of the tubes and the circuits in which they are used.

then goes out every half-cycle while the anode is negative. It will start during the next half-cycle only if the grid potential is above its critical value. Thus, with a circuit such as is shown in Fig. 13-8, for example, when there is no photoelectric current the grid will be negative and no current will be carried by the thyratron. As the photocurrent increases, the grid becomes more positive; and when the critical value is reached the discharge will start and a pulsating direct current will flow in the anode circuit. If the photocurrent is now gradually decreased, the grid potential will fall below its critical value. The next time the anode potential passes through zero the discharge will stop and will not restart. The tube thus acts as an on-and-off relay with a very high power amplification and with practically no hysteresis.

Continuous control may be obtained by operating the grid on alternating current also, with a device for shifting the phase of the grid voltage. With the grid and anode voltages in phase, the discharge will pass during the positive portion of each cycle. When they are out of phase, then, when the anode is positive, the grid may be sufficiently negative to prevent the arc from starting and no current will flow. For intermediate phases the current will flow only during that portion of the cycle when the anode is positive and the grid also sufficiently positive to allow the arc to start. The *average* anode current may then be varied from zero up to the maximum value attained when the two are in phase.

The phase shifting may be accomplished with a photoelectric cell by means of the circuit shown in Fig. 13-9. When there is no light falling on the cell, its resistance is practically infinite, and the anode and grid voltages will be 180 deg out of phase, so that no anode current will flow. As the illumination of the cell is increased, its resistance decreases and, since the cell is connected between anode and grid, will bring the grid voltage more nearly into phase with the anode voltage and cause the anode current to increase. The relation between thyratron current and the illumination of the photoelectric cell is shown in Fig. 13-10 for three different values of the ratio C_2/C_1, where C_1 is the combined capacity between grid and plate of the thyratron and between cathode and anode of the cell, while C_2 is the external capacity in the grid circuit.

Since the current passed by the thyratron may be several amperes, it serves as an excellent relay which can be controlled directly by the photoelectric current. (With very feeble photocurrents, amplification may be used.) A more detailed discussion of its possible uses has been given by Hull.[1] The grid-glow tube may be used in a manner similar to the thyratron.[2]

[1] A. W. Hull, *Gen. Elec. Rev.*, **32**, 213 and 390 (1929).
[2] D. Knowles, *Elec. Jour.*, **26**, 176 (1928).

THE TRANSMISSION OF PICTURES AND SOUND

We come now to a brief discussion of several applications of the photoelectric cell which are of interest because of the tremendous commercial importance they seem destined to attain, namely the talking moving picture, the transmission of pictures by wire or radio, and television. In each case the combination of the modern photoelectric cell with the thermionic vacuum tube has made possible the realization of devices which have been the dream of scientists and inventors for many years.

All three of these applications depend on the ability of the photoelectric cell to respond accurately to light variations of very high frequency (*e.g.*, up to 100 kilocycles). Since, in the applications previously discussed, the photoelectric cell has had to respond only to steady light or to variations of relatively low frequency, it becomes necessary to inquire into the characteristics of cells when used under these conditions.[1]

13-8. Dynamic Characteristics of Photoelectric Cells.—It will be recognized at once that, on account of the instantaneity of the photoelectric effect itself and the high velocity with which the electrons travel from the cathode to anode, the frequency of the light variations to which a vacuum photoelectric cell can respond will be in general limited only by the inductance and capacity of the cell and the accompanying circuit. The photoelectric current from such a cell will therefore follow accurately variations in light intensity up to radio frequencies.

However, in most commercial applications, it is necessary to take advantage of the additional sensitivity of the cell, which can be obtained by gas filling. It is not at once obvious whether the response to high-frequency light variations will be as accurate in such a cell. Experiment shows, in fact, that the ratio of the amplitude of the photocurrent to the amplitude of the light variations decreases as the frequency is increased up to values of the order of several thousand per second. A typical "frequency response" curve is shown in Fig. 13-11.[2] There are apparently two chief factors which contribute to give the smaller response at high frequencies. These are: (1) the fact that in gas-filled cells part of the current is carried by positive ions, which have a lower mobility than electrons, and hence require an appreciable time to travel to the cathode; (2) the fact that, in addition to the electrons released at the cathode by the light, there are also some ejected by the impinging positive ions.

In regard to the first factor, the time taken for a positive ion, say of helium, to travel from anode to cathode, may be easily computed from

[1] After this chapter was written a paper by V. K. Zworykin entitled "Photocell Theory and Practice" appeared in the *Jour. Franklin Inst.*, **212**, 1 (1931).

[2] Taken from Zworykin and Wilson, "Photocells and Their Application," p. 81.

the known mobility, which is 3 cm/sec for a field of 1 volt/cm at a pressure of 760 mm. At a pressure of 0.2 mm used in a gas-filled cell, and a field of 10 volts/cm, the ion velocity will be 1.14×10^5 cm/sec. Hence the time taken to travel between the electrodes of an ordinary cell would be of the order of 10^{-5} sec. An apparent time lag would then be noticed as the frequency approached values in the neighborhood of 100,000 cycles, but this would not account for an appreciable distortion at frequencies less than 10,000.[1]

A further time lag would, however, be introduced if the second process above takes place. Then, for example, if the light were suddenly cut off, the current would continue to flow, due to positive ions ejecting electrons from the cathode, and these electrons in turn producing more

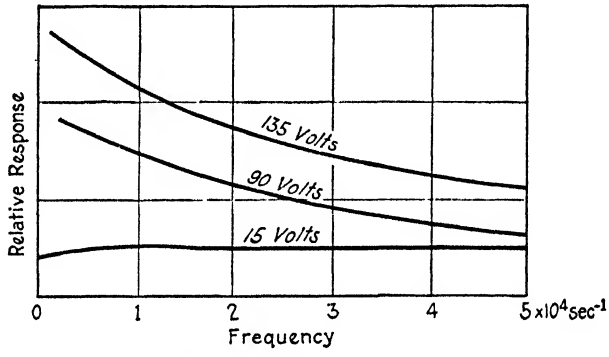

FIG. 13-11.—Response of gas-filled photoelectric cell at various voltages to interrupted illumination.

positive ions, and so on. Since little is known as to the efficiency of positive ions in ejecting electrons from photoelectric cathodes, it is difficult to make quantitative estimates as to how long an appreciable current would continue. It is evident, however, that it would fall off exponentially[1] (and also grow exponentially when light is admitted to the cell) and it appears, according to Zworykin,[2] that this effect may account qualitatively for the observed dynamic characteristics.[3]

Photoconductive and photovoltaic cells are of course less suited for operation at high frequencies than even the gas-filled photoelectric cells,[4] since in both cases there is an inherent time lag in the effect itself.

[1] *Cf.* N. R. CAMPBELL and L. G. STOODLEY, "Discussion on Photoelectric Cells," p. 64.

[2] ZWORYKIN and WILSON, "Photocells and Their Application," p. 81.

[3] Since this section was written a paper by W. F. Tedham entitled "Ionization in Gas-filled Photoelectric Cells" has appeared (*Phil. Mag.*, **12**, 224 [1931]).

[4] In this book we have tried to use the term "photoelectric cell" in its original significance, *i.e.*, referring to a cell in which light causes an emission of electrons from a metal surface. The term "photocell" is sometimes employed to include all these types of cells: "photoelectric," "photoconductive," and "photovoltaic." The

Nevertheless, selenium cells of recent design show a dynamic response sufficiently uniform over frequencies less than 5000 cycles to make them usable in sound reproduction.[1] The same claim is made by manufacturers of certain photovoltaic cells.[2]

In the applications to be discussed below, use is made of this ability of the photoelectric cell to respond to light variations of high frequency. The resulting photoelectric current accurately reproduces the variations in light intensity. Any of the highly perfected methods of alternating-current amplification may then be employed to amplify these variations up to currents of usable magnitudes. A very simple circuit of this type, suitable for many purposes, is shown in Fig. 13-12.

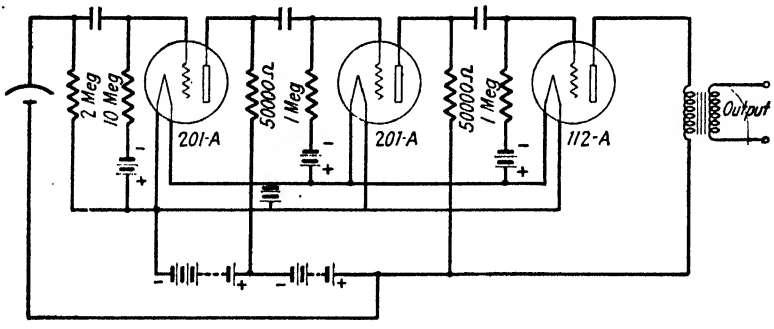

FIG. 13-12.—Three-stage amplifier for interrupted photoelectric currents.

13-9. Talking Moving Pictures.—In certain types of talking pictures the sound is recorded photographically on the film in such a way that an exposed strip either of variable density, or of variable width, runs along one edge of the film. These variations follow the changes in intensity and pitch of the original sound. In the projection machine an intense beam of light is focused on to a very fine slit perpendicular to the direction of motion of the film and a reduced image of this slit is focused on the film. The light transmitted by the film falls on to a photoelectric cell connected to an amplifier and loud-speaker (Fig. 13-13). The amount of light transmitted depends of course on the density, or width, of the exposed sound record, so that as the film passes the beam the variations in light intensity falling on the cell cause the original sound to be reproduced in the loud-speaker. In order to reproduce audible frequencies up to 8000 per second there will be appreciable variations in density in the sound record over distances of the order of 0.003 in. Hence the image of the slit on the film cannot exceed 0.001 in. in width, which greatly restricts the amount of light entering the photoelectric cell.

term "phototube" has come into wide use among engineers to designate the photoelectric cell.

[1] See H. THIRRING, "Discussion on Photoelectric Cells," p. 201.

[2] *E.g.*, the "Arcturus Photolytic Cell."

The power amplification required for this purpose is, of course, enormous. It requires from 10 to 50 watts to operate the loud-speakers in a large theater, and this power must be controlled by photoelectric currents of a few microamperes or less. Gas-filled caesium-on-silver cells are widely used for this purpose.[1]

It is only a step from the audible moving picture to a photoelectric phonograph, in which the sound is recorded on a loop of film instead of

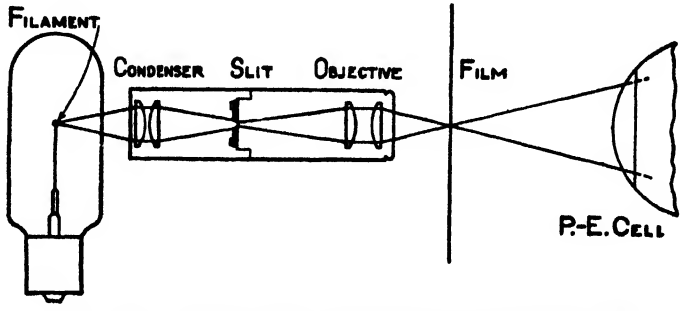

Fig. 13-13.—Optical system for reproduction of sound films.

on a wax record, and the reproduction is by the photoelectric process described above. The advantage claimed for this method is that by running several sound records in parallel on standard-size film it should be possible to reproduce an entire symphony, for example, without changing records.

13-10. Transmission of Pictures.—The photoelectric cell plays an important rôle in any system for the transmission of pictures by wire

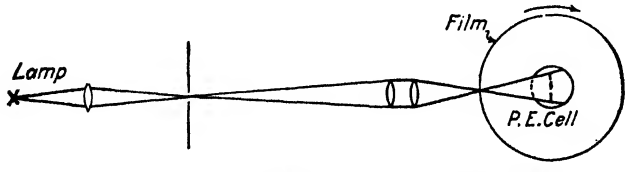

Fig. 13-14.—Optical system for picture transmission.

or by radio ("facsimile transmission")—processes which during the past few years have found wide commercial applications, particularly in the rapid transmitting of news photographs. Here again the principles involved are fairly simple, although the actual apparatus may be exceedingly complex. Figure 13-14 shows a simplified diagram of the apparatus at the sending end of the transmission system developed at the Bell

[1] For further details see Zworykin and Wilson, "Photocells and Their Application," p. 125; and Franklin, "Sound Motion Pictures" (Doubleday, Doran & Company, Inc.).

Telephone Laboratories by Ives and his associates.[1] The film containing the record of the picture to be transmitted is mounted on a cylinder which rotates and at the same time progresses slowly along its axis. A fine beam of light focused on the film thus "scans" a fine helix on the cylinder. The light transmitted by the film falls on a photoelectric cell and during the rotation produces a varying current which is first amplified and then used to modulate a carrier wave suitable for transmission along wires or by radio. Light reflected from an opaque positive picture may be used instead of that transmitted by a negative film. At the receiving end the incoming currents are again amplified and then used to operate either a neon glow tube or an electromagnetic light valve. The latter consists of a metal ribbon carrying the amplified current from the distant photoelectric cell, the ribbon being placed at right angles to a magnetic field. The current variations cause the ribbon to move at right angles to the field, and to its own length, and in so doing to intercept a varying portion of a light beam. In the case of the valve as well as with the neon tube, the varying light beam falls on a sensitized film which is mounted on a cylinder rotating in synchronism with the cylinder carrying the picture at the sending station. The lights and shadows of the original picture are thus reproduced. As in most other commercial developments, the rôle played by the photoelectric cell is quite simple and fundamental. The subsidiary equipment required for amplification, transmission, receiving, synchronization, etc., may, however, be exceedingly complex.

13-11. Television.—In facsimile transmission a single still picture is transferred from an exposed negative at the sending end to a sensitive film at the receiving station. The transmission of a picture 5 by 7 in. normally requires about 7 min. In television, on the other hand, the image of an actual moving scene is transmitted instantaneously to a distant screen so that an observer watches a given event while it is taking place. While fundamentally these two problems are similar in nature, it is evident that television will require the solution of much more serious practical difficulties. For, in the first place, the light intensity which is diffusely reflected from a natural object—even when brilliantly illuminated—is less by a factor of many thousand than that available when an intense beam passes through a transparent film. In the second place in order to give the observer the illusion of continuous motion, it is necessary that a complete image of the distant scene be reproduced on the screen about sixteen times each second. In order to give an image sufficiently fine-grained to be recognizable, it is evident that the photocell and amplifier must be sensitive to light variations

[1] Ives, Horton, Parker, and Clark, *Bell Syst. Tech. Jour.*, **4**, 187 (1925); also Ives, *Jour. Opt. Soc. Amer.*, **15**, 96 (1927); F. Schröter, *Zeits. f. Tech. Phys.*, **7**, 417 (1926).

of exceedingly high frequencies—of the order of 60,000 cycles in actual practice—as well as to frequencies as low as 16 per second. This is a range of over 12 octaves, compared to the 6 octaves usually considered sufficient for good audio reproduction.

Figure 13-15 shows the general scheme employed in the television system developed by the Bell Telephone Laboratories.[1] The beam-scanning method is employed in which an intense beam of light from an arc passes through a hole in the scanning disk and is focused on to the object whose image is to be transmitted. The holes in the disk are arranged in a spiral so that, as the disk rotates, the beam scans a series of lines across the object, each slightly displaced from the previous one. The entire object is scanned sixteen times each second. The diffusely reflected

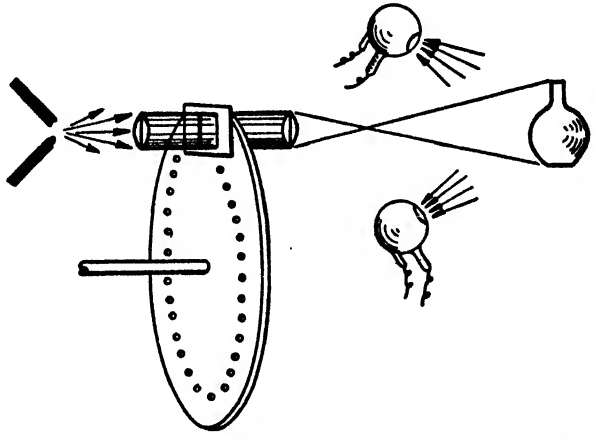

FIG. 13-15.—Direct scanning method used in television.

light is collected by a bank of photoelectric cells so constructed as to present the largest possible sensitive area to the light. At any instant the light received by the photocells comes from only a single spot on the illuminated object, and as the scanning beam moves, the lights and shades of the object are transformed into rapidly varying photocurrents. These are amplified enormously and used to modulate a carrier frequency suitable for transmission over wires or by radio.

At the receiving end the incoming signals, after amplification, are used to operate a neon glow tube, and so are transformed back into variations in light intensity. If the neon glow is viewed through a rotating disk similar to the disk at the sending station, and rotating in synchronism with it, the image may be seen. A successful television system has been devised by Alexanderson[2] in which at the receiving end the incoming

[1] Symposium on Television, *Bell Syst. Tech. Jour.*, 6, 551 (1927).
[2] According to an item in *Electronics*, 1, 147 (1930).

signals, instead of operating a neon tube, are applied to the electrodes of a Kerr cell.[1] This serves to modulate the intensity of a light beam from an arc, so that the televised image may be projected on a screen of sufficient size to be seen by a large audience.

The photoelectric cells developed at the Bell Telephone Laboratories for television purposes are of some interest. They are sensitized potassium gas-filled cells of a tubular shape, having a total length of 14 in. and a diameter of 4 in., so that there is a total cathode area of approximately 40 in.^{2}. Three such cells, connected in parallel, were used in the sending outfit described.

In other television transmitting sets which have been devised instead of using photocells of large area, large parabolic reflectors were used to concentrate the light on small cells.[2] The technique of television transmission is undergoing rapid development, and any more detailed account of the methods used would be obsolete almost as soon as it was written. The rôle played by the photoelectric cell, however, is fundamental, and the advances to be expected will have to do largely with increasing the sensitivity of the cells and speed of the optical systems and, more particularly, with increasing the efficiency and simplicity of the subsidiary equipment for amplification, modulation, transmission, receiving, etc.[3]

13-12. Miscellaneous Applications.—Lack of space forbids detailed descriptions of many other interesting and useful photoelectric devices. A few of those of especial interest which have come to our attention are given for reference in the following list.

Photoelectric measurement of light absorption has found interesting applications in determining the penetration of light into sea water,[4] in the determination of the amount of ozone in the upper atmosphere[5] (from intensity of absorption bands) and in measuring the after-glow in active nitrogen.[6]

The photoelectric cell has been used as a color indicator and automatic control in chemical titration,[7] and has been used to replace the eye in polarimetry.[8] Its ability to measure very feeble light intensities has

[1] E. Schröter, *Elekt. Nach-Tech.*, **6**, 439 (1929).

[2] See Zworykin and Wilson, "Photocells and Their Application," p. 148.

[3] An interesting account of the subjects of television and facsimile transmission will be found in the book "Television," by H. H. Sheldon and E. N. Grisewood (D. Van Nostrand Company, 1929). See also Dinsdale, "Television" (Sir Isaac Pitman & Sons); and many articles in *Electronics*, for 1930 and 1931.

[4] E. O. Hulbert, *Jour. Opt. Soc. Amer.*, **17**, 15 (1928); H. H. Poole and W. R. G Atkins, *Jour. Marine Biol. Assn.*, **14**, 177 (1926); **15**, 455 (1928).

[5] G. M. B. Dobson, "Discussion on Photoelectric Cells," p. 185.

[6] E. von Angerer, *Phys. Zeits.*, **22**, 97 (1921).

[7] R. H. Müller and H. M. Partridge, *Indust. and Eng. Chem.*, **20**, 423 (1928); *Jour. Sci. Instr.*, **6**, 74 (1929).

[8] H. von Halban, *Nature*, **119**, 85 (1927); J. Kenyon, *Nature*, **117**, 304 (1926); C. Todesco, *Nuovo Cimento*, **5**, 376 (1928).

been applied by Lord Rayleigh to the study of light from the night sky[1] and by Przibram to measurements of radio luminescence.[2]

A "summation actinometer," a device for integrating the total ultraviolet energy in sunlight throughout the day, is obtained either by connecting a photoelectric cell to a hydrogen voltameter or by determining the area under an automatically recorded photocurrent curve.[3]

The photoelectric cell has been successfully used as a radiation pyrometer for measurement of color temperatures of hot bodies[4] and has considerable possibilities in the automatic control of furnace temperatures, etc.

Angular deviations of a light beam may be measured to within 0.05 sec of arc by splitting the beam into two parts and determining changes in their relative intensity with a photoelectric cell.[5] This has been applied to the problem of measuring the small deviation of a beam of light in passing through a hollow prism containing a gas whose index of refraction is to be measured.

Linear amplification of a galvanometer deflection may be obtained by using a photoelectric cell to replace the usual thermopile.[6]

If light is allowed to pass through two grids into a photoelectric cell, exceedingly small displacements of one grid, relative to the other, may be measured.[7]

The photoelectric production of accurate time signals by means of a light beam interrupted by a swinging pendulum has already been mentioned.[8] The advantage is of course that this method involves no mercury contacts and produces no mechanical reaction on the pendulum. An escapement for actuating a standard pendulum without any mechanical contact has been devised by R. E. Gould of the U. S. Bureau of Standards. An accurately timed impulse is given to the pendulum every 60 oscillations by means of an electromagnet actuated by a photoelectric cell and relay.[9]

[1] Rayleigh, *Proc. Roy. Soc.*, **124**, 395 (1929).

[2] K. Przibram and E. Kara-Michailova, *Sitz.-ber. d. Akad. d. Wiss. Wien*, **132**, 285 (1924).

[3] L. R. Koller, *Gen. Elec. Rev.*, **31**, 85 (1928); A. S. G. Hill, "Discussion on Photoelectric Cells," p. 138; W. R. G. Atkins and H. H. Poole, *ibid.*, p. 128; *Proc. Roy. Soc., Dublin*, **19**, 159 (1929); *Nature*, **125**, 305 (1930); I. Ranze, *Nuovo Cimento*, **5**, 234 (1928); J. A. C. Teegan and G. R. Randall, *Indian Jour. Phys.*, **4**, 585 (1930).

[4] F. A. Lindemann and T. C. Keeley, *Proc. Phys. Soc. Lond.*, **38**, 69 (1925); Research Staff of the General Electric Company, *Jour. Sci. Inst.*, **2**, 177 (1925).

[5] D. S. Perfect, "Discussion on Photoelectric Cells," p. 106.

[6] F. E. Null, *Jour. Opt. Soc. Amer.*, **12**, 521 (1926).

[7] G. D. Critescu, *Phys. Zeits.*, **30**, 24 (1929); J. A. C. Teegan and K. G. Krishnan, *Phil. Mag.*, **9**, 589 (1930).

[8] J. V. Hoffacker, *Phys. Rev.*, **35**, 121 (1930); J. E. Fox, P. Rood, and W. G. Marburger, *Jour. Opt. Soc. Amer.*, **15**, 364 (1927).

[9] R. E. Gould, private communication (1930); see also G. Ferrie and R. Jouaust, *Comptes Rend.*, **180**, 1145 (1925).

The suggestion has been made[1] that accurate spacing between rulings of a diffraction grating could be obtained, without the necessity of using a high-precision screw, by mounting the movable mirror of an interferometer on the carriage of the ruling engine. A photoelectric cell would then be used to "count" the fringes passing as the carriage is moved between rulings, and automatically set the ruling point in motion when the proper number of fringes had passed.

An ingenious reading device for the blind has been described by d'Albe[2] in which each line of a printed page is scanned by five light beams closely arrayed in a straight line along the height of the printed characters. Each beam is being interrupted at a different frequency by a rotating disk, the frequencies corresponding to five notes on a musical scale. The light is reflected into a photoelectric cell (d'Albe used a selenium cell) the output of which—after amplification, if necessary—is used to operate a pair of headphones (or a loud-speaker). As the light beams pass each printed letter the amount of light reflected varies and a characteristic "tune" is heard in the phones. It is stated that with surprisingly little practice a blind person can learn to read with his ears!

Only a brief mention has been made of the wide variety of ways in which photoelectric cells may be used in the control of industrial processes. They have been found particularly useful for automatic counting, registering or sorting products according to their color, size, reflectivity, etc.[3]

A photoelectric process of making half-tone negatives, applicable to transmission over telephone lines, is described by Ives.[4,5]

[1] The suggestion is quoted in Zworykin and Wilson, "Photocells and Their Application," p. 162, and is credited to Gramont.

[2] E. F. D'ALBE, "The Moon-Element," p. 94 (D. Appleton & Company, 1924).

[3] See, for example, J. V. Breisky, "The Photo-cell in Industrial Processes," *Electronics*, **1**, 227 (1930).

[4] H. E. IVES, *Jour. Opt. Soc. Amer.*, **15**, 96 (1927).

[5] Since this section was written, the following papers on applications of photoelectric cells have appeared: "A Photoelectric Integraph" by T. S. Gray (*Jour. Franklin Inst.*, **212**, 77 [1931]); "A Method of Measuring Integrated Light Intensities" by L. R. Koller (*Rev. Sci. Instr.*, **2**, 551 [1931]).

CHAPTER XIV

MISCELLANEOUS

In this chapter we discuss a number of interesting photoelectric phenomena which are not readily classified under the subjects taken up in the previous chapters. Some of these are of considerable potential importance and would well repay further investigation.

14-1. Photoelectric Current and Film Thickness (Metal).—The effect of varying the thickness of a film of metal upon the velocities of the photoelectrons from it has been discussed in Sec. **4-4.** Here we shall consider the total current emitted from a film as a function of its thickness.

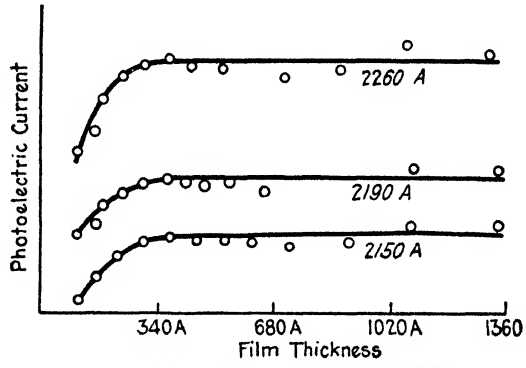

FIG. 14-1.—Photoelectric current as a function of film thickness. (*Werner.*) Metal, gold.

The procedure adopted in general is to prepare a number of films of different thicknesses, usually by cathode sputtering or by evaporation, and to measure the photoelectric current from each. The critical thickness above which the photoelectric current remains unchanged is taken to measure the greatest depth from which the photoelectrons come. Beyond this critical thickness, the film is, photoelectrically speaking, identical with the massive metal. By methods of this sort Rubens and Ladenburg[1] concluded that the path of photoelectrons in gold foil was of the order of 1000A, while Werner,[2] who investigated gold films deposited on glass by cathode sputtering, found the maximum path to be 300A (Fig. 14-1).

[1] H. RUBENS and E. LADENBURG, *Verh. d. Deutsch. Phys. Ges.*, **9**, 749 (1907).
[2] S. WERNER, *Dissertation, Upsala*, 1913.

Stuhlmann[1] prepared his films by evaporation from a wire placed to one side of a quartz plate, thus producing a deposit of decreasing thickness. Inasmuch as different thicknesses, *i.e.*, different parts of the same deposit, were here produced simultaneously, it would appear that this method had a decided advantage over those methods in which different thicknesses were produced at different times, where accidental slight variations in the conditions of sputtering or evaporation would tend to make the successive films not strictly comparable with each other. The results for platinum and silver are shown in Fig. 14-2. It will be seen that the photoelectric emission at first increases with the thickness, then over a certain range of thickness it actually diminishes as the thickness is increased, and finally begins to increase again with the thickness. It is possible that the appearance of the maximum and minimum at

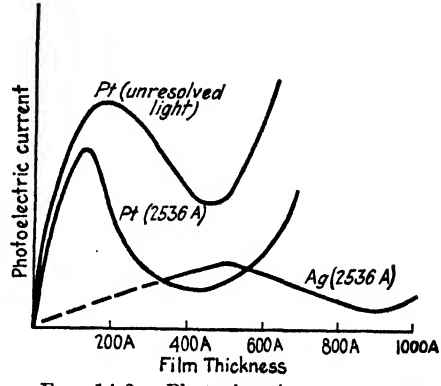

FIG. 14-2.—Photoelectric current as a function of film thickness. Evaporated platinum and silver films.

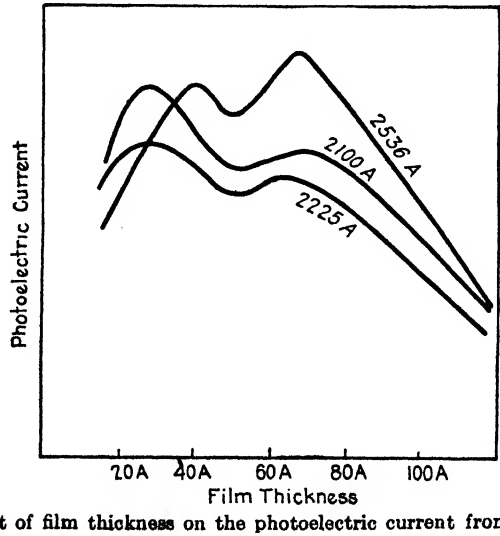

FIG. 14-3.—Effect of film thickness on the photoelectric current from platinum films on glass.

smaller thicknesses for platinum than for silver may be related to the fact that the absorption coefficient for light is greater in the former than in the latter.

[1] O. STUHLMANN *Phys. Rev.*, **19**, 132 (1919); **20**, 65 (1920).

Compton and Ross[1] studied sputtered films of platinum and gold. Three distinct methods were used to determine the thickness of a film and gave values in satisfactory agreement. A typical set of curves is shown in Fig. 14-3. They differ radically from those given by Stuhlmann in that there are two maxima, and in that there is no agreement between the location of the maxima found by them and those found by Stuhlmann. The second maximum (for the greater thickness) disappears in the course of time. It therefore seems to be associated with some form of instability (gas layers ?) in newly sputtered films. They calculated the relation between the photoelectric current and the thickness of the film on three

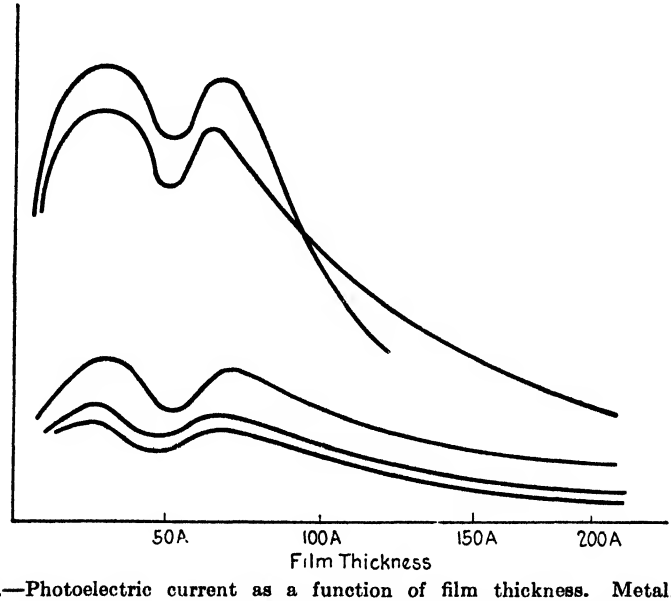

FIG. 14-4.—Photoelectric current as a function of film thickness. Metal, platinum (sputtered). The five curves are for five different wave-lengths.

different assumptions. These were as follows: (1) that the number of electrons which retain ability to escape falls off exponentially with the distance moved through perpendicularly to the surface, (2) that the number which retain ability to escape fall off exponentially with the distance moved through in *any* direction, and (3) that an electron loses energy in proportion to the distance moved through in a metal. The results fitted both 1 and 2 but not 3. (The formulas were tested by the portions of the curves in the vicinity of the first maximum.) Electronic mean free paths of 2.67×10^{-7} and 5.0×10^{-7} cm were obtained for Pt and Ag, respectively. The most important result of this work perhaps is that the ability to escape is the same for a fast electron (*i.e.*, one produced by the highest frequency) as for a slow electron. This can only be accounted

[1] K. T. COMPTON and L. W. ROSS, *Phys. Rev.*, **13**, 295 (1919).

for on the assumption that an electron loses its energy completely at one collision; otherwise the faster one would travel farther.

Dember and Goldschmidt[1] repeated Compton and Ross's work with certain refinements. To determine the amount of light really effective in each film they measured experimentally the amount of light actually absorbed in the film. (The optical absorption constants so found are considerably greater than those calculated from the optical properties of the massive metal.) Figure 14-4 shows that the double maxima appear at the same values of the film thickness regardless of the wave-length used. They also confirmed the result that the mean free path of the photoelectron is independent of its initial speed (or of the frequency of the light producing it). The value of the mean free path of the photoelectrons in platinum, according to their experiments, amounts to 1.08×10^{-7} cm.

It is evident from a consideration of Figs. 14-1, 14-2, 14-3, and 14-4 that there is very little agreement as to the photoelectric behavior of thin films. There is a certain qualitative correspondence between the results shown in Figs. 14-3 and 14-4, in that each curve has two maxima at approximately the same locations. The presence of two maxima suggests that it may be possible to account for the peculiarities in the photoelectric currents from these films on lines similar to those used by Akulov and Hlucka to account for a succession of maxima and minima in the photoelectric currents from films of certain dyes as the thickness of the film was increased (Sec. **10-6**).[2]

14-2. Formation of Visible Images on the Cathodes of Certain Photoelectric Cells.—Olpin and Stilwell[3] discovered that it was possible to change the color of the cathodes of certain photoelectric cells by illumination. For example, a lamp filament may be focused on to the sensitive surface by means of a lens with the result that, if the conditions be just right, the image will be recorded as a permanent or semipermanent change of color. This effect occurs only with certain cells containing cathodes whose surfaces are "composite." Typical surfaces showing this effect are those of sodium or potassium which have been sensitized by exposure to sulphur, air, bromine, etc. (Sec. **5-11**). It will be recalled that a high photoelectric emission requires a delicate adjustment of the amount of the sensitizing material to that of the alkali metal and also that the outermost layer should be a monatomic film of metal. The conditions for the appearance of the photographic effect—as this new effect discovered by Olpin and Stilwell may be called—are much more critical

[1] H. Goldschmidt and H. Dember, *Zeits. f. Tech. Phys.*, **7**, 137 (1926).

[2] Since this section was written, the following papers related to it have appeared: "Some Photoelectric Properties of Mercury Films" by D. Roller, W. H. Jordan, and C. S. Woodward (*Phys. Rev.*, **38**, 396 [1931]); "The Photoelectric Effect in Thin Metallic Films," by W. G. Penny (*Proc. Roy. Soc.*, **133**, 407 [1931]).

[3] A. R. Olpin and G. R. Stilwell, *Jour. Opt. Soc. Amer.*, **21**, 177 (1931).

even than those for appearance of the maximum photoelectric effect. When the surface is in the critical condition, exposure to light produces a visible change in color. As an example of this we may cite that the color of a potassium surface treated by hydrofluoric acid is yellow, but after exposure it changes to deep brown. The photoelectric emission from such a surface, after sufficient exposure to white light to change its color, decreases by about 30 per cent. In the course of a few days the color fades away, but the photoelectric emission remains unchanged at the diminished value. Experimentally, the most convenient way of avoiding the necessity for securing the stringent conditions for obtaining the photographic effect is to illuminate the cathode steadily while the sensitizing substance is being admitted very slowly. The surface will pass through the critical state sooner or later and, even though it lasts for but a very short time, the photographic effect will occur.

Let us now consider a possible explanation. It will be recalled that certain crystals (*e.g.*, rocksalt and silver bromide) before being exposed to light have a characteristic absorption band (Sec. **8-23**). Absorption of sufficient light in this band causes the appearance of an induced absorption band on the long wave-length side of the characteristic band. In the case of rocksalt, the colorless crystal becomes greenish yellow, while in the case of silver bromide the latent image is formed. It is possible that the change in color, observed by Olpin and Stilwell, is due to the formation of an induced absorption band in the minute crystals forming the composite surface layer. (That such crystals do exist in a potassium surface merely exposed to hydrogen has been shown by Kluge and Rupp [Sec. **5-10**].) The absorption of light in this new induced absorption band causes either reversible excitation or irreversible bleaching, or perhaps both (Sec. **8-23**). Possibly the subsequent slow fading of the color, induced in these composite cathodes, may correspond to the bleaching observed in certain crystals, that is, to the disappearance of the induced absorption band when the crystals referred to are illuminated by infra-red light.[1] It was stated in Sec. **8-23** that a much closer correlation had been found between induced absorption-band phenomena and photoconductivity than between these and the surface photoelectric effect. But, as it is impossible to carry out photoconductivity experiments within the material of the surface layers of these composite cathodes, it is perhaps permissible to assume that the changes in the surface photoelectric effect may indicate parallel changes in the photoconductivity. In this way we see a reason for a possible association between the color changes observed by Olpin and Stilwell and the diminution in the surface photoelectric effect, although it is not clear even what the sign

[1] It is assumed in the absence of an explicit statement to the contrary that the photoelectric cells were not kept in the dark and thus the "fading" may be attributed to the bleaching effect referred to.

of the correlation should be. The problem is undoubtedly a complicated one. The characteristic absorption band and the induced absorption band may overlap considerably as in the case of silver bromide and, since white light was used in these experiments, we may have the formation and destruction (*i.e.*, the bleaching) of the induced absorption band going on simultaneously. How much photoconductivity to associate with each of the two bands we do not know. The surface photoelectric effect contains, on the simplest picture, one more factor than the photoconductivity, and this is the surface work function which may itself change with the changes induced in the material. It is clearly a formidable task to trace out a quantitative connection between the change in color of the cathode and its surface photoelectric effect. Yet these experiments are significant in that they are among the first to indicate a connection between the surface photoelectric effect and some of the photoconductivity phenomena unraveled by Gudden and Pohl.

It was stated that the dark areas on the surface produced by the light faded out in a few days. These can be "fixed" permanently merely by exposing the surface to the sensitizing vapor for a little longer than is necessary to obtain the critical condition. Moreover, a condition called "reversal" by Olpin and Stilwell, because the illuminated areas become lighter in color than the unilluminated, can be obtained by exposing the surface on which the image has been produced first to the sensitizing vapor and then to the alkali-metal vapor, and repeating this sequence several times.

14-3. Diminution of Photoelectric Emission by Simultaneous Infra-red Illumination.—Certain cells containing composite surfaces of the type referred to in the previous section have been found to show a remarkable decrease in photoelectric emission, amounting sometimes to about 50 per cent, when they are illuminated by infra-red light (Olpin[1]). This effect is probably limited to what we have termed composite surfaces, *i.e.*, to alkali-metal surfaces which have been suitably exposed to some dielectric material such as bromine or iodine. As in the previous section, we may assume that the significant factor here is that the surface layer is a layer of insulating or partially insulating crystals of a compound of the alkali metal. Applying the ideas developed in Sec. **8-23**, absorption of light in the characteristic absorption band of this layer produces an induced absorption band. This induced absorption band may extend far into the infra-red, *i.e.*, to a considerable distance beyond the threshold of the *surface* photoelectric effect. We have seen that the absorption of light in the induced absorption band leads in many cases to an irreversible "bleaching," *i.e.*, to the disappearance of the induced absorption band.[2] If such an effect occurs here, flooding the surface with infra-red

[1] A. R. Olpin, *Phys. Rev.*, **36**, 376 (1930).

[2] With some crystals, absorption of infra-red light merely results in the removal of excitation. We believe, however, that the bleaching effect is the proper one to consider in the case under discussion.

light would diminish the intensity of the induced absorption band and so decrease the photoconductivity associated with it. If we assume that the surface photoelectric effect occurring on the short wave-length side of the threshold is closely related to the photoconductivity, and changes with it, we have a reason for the phenomena observed by Olpin. This view is in harmony with the experimental result that the effect is most strongly marked when the photoelectric effect is produced by light whose wave-length is not far removed from the threshold. Absorption of blue or ultra-violet light would probably take place in the characteristic absorption band whose strength, unlike that of the induced absorption band, is unaffected by the presence of infra-red light. Hence the associated photoelectric effect would be independent of the presence or absence of infra-red light. As Olpin points out, the effect is analogous to the quenching of phosphorescence and to the destruction of the latent image by infra-red light.

14-4. The Shenstone Effect.—Shenstone[1] discovered that the photoelectric emission from a bismuth plate in a vacuum increases considerably after an electric current has been passed through it. In one particular case, which may be cited as typical, increasing the current through the bismuth to a value of about 1.0 amp produced no measurable change in the photoelectric emission, but, beyond this point, increasing the current step by step produced a regularly increasing photoelectric emission. An increase in the latter of about 50 per cent was obtained with a current of 3.0 amp. (The emission could be measured when the current was on, or immediately after it was shut off.) It was suggested by Horton[2] that the change in the photoelectric emission was due merely to the heating effect of the current changing the amount of adsorbed gas. Later experiments made by Shenstone could not be reconciled with this view. In the first place, when the experiment was carried out in such a way that the same change of temperature ($< 25°C$) as that produced by the current was produced by a method not involving a current, no increase in the photoelectric emission could be observed. In the second place, when a current was passed through a metal film deposited on a glass tube kept cool by running water, a large increase in the photoelectric emission was obtained, although the temperature change was negligible. Several other metals (copper, silver, gold, and nickel) showed effects somewhat similar to that described for bismuth. Considerable time lags in the phenomenon were observed. Thus, after the current was shut off, the photoelectric emission would diminish during the course of an hour or more to about the value it had before the current was passed through the metal. So far as we know, no satisfactory

[1] A. G. Shenstone, *Phil. Mag.*, **41**, 916 (1921); **42**, 596 (1921); **45**, 918 (1923).
[2] F. Horton, *Phil. Mag.*, **42**, 279 (1921).

explanation has been proposed for these results, and while several recent observers have measured the photoelectric emission from electrically heated specimens, none has reported any indication of the Shenstone effect.

14-5. Effect of Light on the Secondary Electron Emission from Metals.—It is well known that when a metal plate is bombarded with electrons (say from a hot filament) secondary electrons are ejected from the plate with velocities ranging from zero up to the velocity of the bombarding beam. In some cases the number of electrons leaving the plate is greater than the number striking it. In 1925, Dember[1] found that when the metal plate is illuminated the number of secondary electrons is increased by an amount which is greater than the pure photoelectric current produced by the same light when the plate is not bombarded. Or, stated in another way, the photoelectric current from the plate is increased by the bombarding electrons.

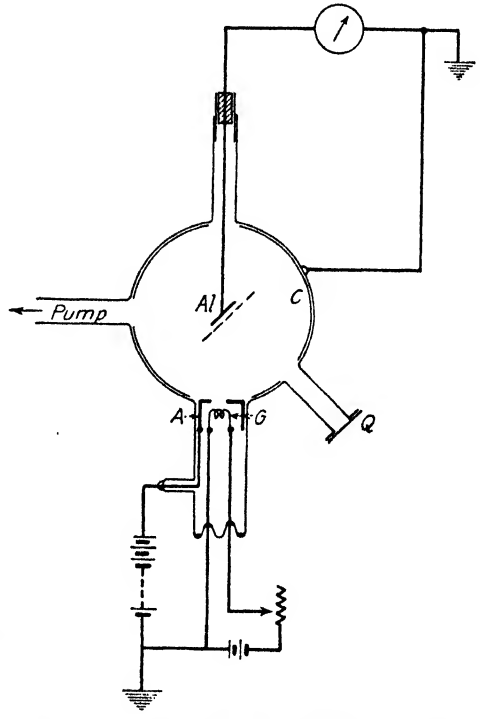

FIG. 14-5.—Dember's apparatus. *Al*, aluminum plate. *Q*, quartz window. *G*, filament. *A*, anode. *C*, collector.

The apparatus used by Dember is shown in Fig. 14-5. The aluminum plate *Al* may be illuminated by light entering through the quartz window *Q* and may be bombarded by electrons from the hot filament *G* which may be given any velocity by applying a potential to the anode *A*. The secondary electrons are collected by a silver coating *C* on the walls of the enclosing bulb, and are measured by the galvanometer. Some of the results are shown in Table 14-1. The first column shows the pure photoelectric current excited by a quartz mercury arc. The second column gives the pure secondary electron current with the light off; the third column gives the secondary current with the light on; the last column gives the difference between 3 and (1 + 2). The voltage between *G* and *A* was 98 volts and there was no field between the plate and the collecting electrode. The successive values in the table are for increasing values of the primary bombarding current.

[1] H. DEMBER, *Zeits. f. Phys.*, **33**, 529 (1925).

TABLE 14-1.—SECONDARY ELECTRON CURRENTS

I	II	III	IV
Pure photoelectric current *	Pure secondary current *	Secondary current with light on	Increase III − (II + I)
40	3	55	12
40	21	90	29
40	308	869	521
40	4,455	8,745	4,250
40	7,070	13,029	5,919
40	197,000	201,000	3,960

* The unit in each case is 2.24×10^{-10} amp.

It will be seen that the increased current produced by the light rises to a maximum and then falls as the primary bombarding current is increased, and the maximum value is about 150 times the pure photoelectric current. For a fixed primary current it was found that the extra light currents increased with the intensity of the light but approached a "saturation" value. By inserting filters in the light beam it was found that an increase was produced by all wave-lengths out to the red end of the spectrum, although the threshold for the aluminum when not being bombarded was near 3340A.

The effect is an interesting one and seems to be analogous to the increase produced by light in the thermionic current from composite surfaces discussed in Sec. **3-29.** In each case there are some electrons within the metal which lack the full energy required to escape, and which attain the required energy from the light beam. Even red light may furnish sufficient energy to enable some of the electrons to escape. Both of these effects may well repay further investigation, since they may be of use in "sensitizing" photoelectric cells.

14-6. Are Positive Rays Produced by Ultra-violet Light?—Dember[1] in 1909 reported on an experiment which seemed to show that light falling on a metal surface produced, in addition to the ordinary electron emission, a very small emission of positive ions. In this experiment light was allowed to fall on a perforated metal plate A (Fig. 14-6), and the photoelectrons were collected by the positively charged grid B. Behind the plate A was placed a receiving electrode C which was connected to an electrometer. It was found that, when A was illuminated by ultra-violet light and given a small positive potential with respect to C, the electrometer acquired a positive charge. This was attributed to positive ions ejected from A which passed through the perforations (like canal rays) and reached C. Since the effect was observed at low pressures and for accelerating voltages of less than 5 volts it could not be

[1] H. DEMBER, *Ann. d. Phys.*, **30**, 137 (1909).

ascribed to ions produced by collision of the photoelectrons with gas atoms. The possibility that the positive currents were due to photoelectrons *leaving* C under the action of scattered light reaching it was rejected on the ground that the positive currents depended on the potential difference between A and B, as well as on that between B and C, while it was thought the emission of photoelectrons from C should be independent of the field between A and B.

Such an emission of positive ions under the influence of light would of course be a phenomenon of great interest in photoelectricity. However, Dember's experiments were repeated in 1925 by one of the authors[1] under conditions which allowed a more complete control of scattered light within the tube and a greater variability in manipulating the electric

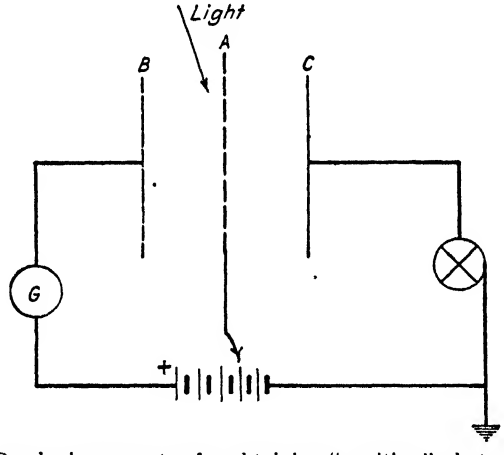

FIG. 14-6.—Dember's apparatus for obtaining "positive" photoelectric effect.

fields between the various electrodes. The receiving electrode was completely surrounded by a cylinder which, when given a negative potential, would prevent the emission of photoelectrons. With the cylinder and plate at the same potential, positive currents similar to those obtained by Dember were in fact observed. But they persisted when the illuminated plate was given a large negative potential to prevent positive ions leaving it, and the effect disappeared when the cylinder was negatively charged. It was quite evident that the currents were therefore due to scattered light reaching C and releasing photoelectrons. These currents were found to depend on the field between A and B because of the fact that this field actually penetrated into the region between B and C, a phenomenon well known to users of radio tubes. When the scattered light currents were eliminated, no true positive-ion currents could be detected, although the electrometer would have registered a current as small as 2×10^{-17} amp. It was concluded that there was no

[1] L. A. DUBRIDGE, *Phys. Rev.*, **25**, 201 (1925).

measurable photoelectric production of positive ions at metal surfaces. This result was obtained for the three metals gold, copper, and aluminum in the form of solid plates and sputtered films, and did not depend on whether the plates had or had not been previously outgassed. A similar result was also obtained by Butterworth[1] for potassium surfaces, who found that if such currents existed they must be 10^7 times smaller than the ordinary photoelectron currents.

Wasser[2] and Hake[3] have reported that microscopic droplets of mercury, paraffin, selenium, glycerin, etc., as used in a Millikan condenser for measuring the electronic charge, were occasionally observed to acquire a negative charge under the influence of ultra-violet light. This was attributed to the ejection of positive ions from the droplets. (This has often been referred to as the "inverse photoelectric effect," an unfortunate term, since the inverse of the photoelectric effect is the production of radiation, *e.g.*, X-rays, by electrons.) In 1926, however, Lorenz[4] examined this question with some care and concluded that there was no true positive photoelectric effect, the negative charges on the droplets being acquired by the capture of free electrons which had been photoelectrically released from the condenser plates. Still later, Scharf[5] reported that he was unable to observe a true positive-ion ejection for ordinary-sized droplets, but that if the droplets were smaller than about 10^{-5} cm in diameter they did occasionally acquire negative charges. There seems to be no reason to suppose that the effect should be different for drops of different sizes, however, and one is inclined to ascribe the results to some spurious effect which may be exceedingly difficult to eliminate.

The *thermionic emission* of positive ions is a well known effect which has been extensively studied.[6] Analysis of the ions emitted from metals at high temperatures has shown that in general they are gaseous, or more commonly, ions of the alkali metals. Recently, Wahlin[7] and Smith[8] have found that certain metals at high temperatures give off ions of the metal itself. The emission of foreign ions is quite copious for fresh metal specimens (at low temperatures many times larger than the ordinary electron emission) but shows a marked decay with time as the specimen is heated. From the analogy between thermionic and photoelectric emission it might be expected that positive ions would also be ejected from metals by light. (It is known[9] that ultra-violet light *does* cause the removal of gases from some metals, though the experiments discussed above seem to indicate that the gas atoms are not ionized when they come off.) The reason that a positive photoelectric emission

[1] J. Butterworth, *Phil. Mag.*, **6**, 1 (1928).
[2] E. Wasser, *Zeits. f. Phys.*, **27**, 203 (1924).
[3] M. Hake, *Zeits. f. Phys.*, **15**, 110 (1923).
[4] E. J. Lorenz, *Phil. Mag.*, **1**, 499 (1926).
[5] K. Scharf, *Zeits. f. Phys.*, **49**, 827 (1928).
[6] See O. W. Richardson, "Emission of Electricity from Hot Bodies," (Longmans, Green & Co., 1921).
[7] H. B. Wahlin, *Phys. Rev.*, **34**, 164 (1929).
[8] L. P. Smith, *Phys. Rev.*, **34**, 1496 (1929).
[9] R. P. Winch, *Phys. Rev.*, **36**, 601 (1930); also a private communication.

does not occur is probably that the energy which can be absorbed by an atom in an elastic collision with a quantum of ultra-violet light is too small to allow its removal from the surface as an ion.

14-7. Effect of Magnetic Fields on Photoelectric Emission.—Dember[1] has reported an experiment in which an attempt was made to determine whether the photoelectric sensitivity of a plate of bismuth was altered by applying a magnetic field normal to the plate. The plate (6 mm in diameter) and a parallel collecting grid were mounted in a small evacuated tube placed between the poles of an electromagnet, the illumination being normal to the plate through a hole bored in one pole piece. When the accelerating voltage between plate and grid was only 0.07 volt the photoelectric sensitivity to a mercury arc diminished by approximately 39 per cent when the magnetic field was increased from 0 to about 6800 gauss. But when the accelerating field was 270 volts the decrease was only 1.8 per cent. This effect is thus apparently due to an effect on the electrons after they leave the bismuth plate, and not to an effect on the photoelectric process itself. It was found that the percentage change in current produced by a given magnetic field increased as the temperature of the system was lowered to $-79°C$, though with the small accelerating fields used this might be due to a change in contact potential between the plate and collecting grid (of brass).

Polvani[2] has found the photoelectric emission from iron to be independent, within experimental error, of the magnetic induction in the iron up to approximately 10,000 gauss. It thus appears that when sufficiently large accelerating potentials are used to collect the electrons the photoelectric process is not appreciably affected by the presence of a magnetic field.

14-8. The Marx Effect.—Marx[3] has recently reported on an experiment which seems to show that the stopping potential required to prevent the escape of photoelectrons from an illuminated potassium or sodium surface is decreased when the surface is simultaneously illuminated by light of a lower frequency. Under ordinary conditions (as pointed out in Chapter II) the stopping potential is a measure of the energy of the fastest electrons leaving the illuminated surface, and hence should depend only on the *highest* frequency present in the illumination. Any effect due to the presence of light of lower frequency is therefore quite surprising.

In Marx's experiment a layer of potassium was deposited on a platinized glass "mushroom." This was surrounded by a wire ring to serve as an anode and mounted in an evacuated bulb the inside surface

[1] H. Dember, *Phys. Zeits.*, **21**, 568 (1920).

[2] G. Polvani, *Nuovo Cimento*, **24**, 65 (1922).

[3] E. Marx, *Naturwiss.*, **17**, 806 (1930); *Phys. Rev.*, **35**, 1059 (1930); E. Marx and A. E. H. Meyer, *Phys. Zeits.*, **31**, 352 (1930).

of which was also coated with potassium. A negative potential was applied to the anode just sufficient to reduce the photoelectric current—as measured by a string electrometer—to zero. The stopping potential was first determined in this way when the potassium surface was illuminated by light passing through a blue filter. When light passing through an orange filter was also admitted to the cell, the potential required was smaller.

In later experiments two beams of monochromatic light were used and it was found: (1) that the decrease in stopping potential is directly proportional to the intensity of the low-frequency beam, until fairly high intensities are reached; (2) for high intensities of the low-frequency relative to the high-frequency component, the stopping potential approaches the value which would be observed if the low frequency were present alone; (3) the amount by which the stopping potential is decreased is directly proportional to the frequency *difference* between the two beams.

Marx's experiment has been repeated by Olpin[1] under somewhat different conditions. He pointed out that the Marx effect could be accounted for qualitatively if the anode of his photoelectric cell were also photoelectrically sensitive so as to cause a reverse current, and if the anode were more sensitive to red light than to blue. This condition is quite likely to hold owing to the deposition on the anode of a thin red-sensitive potassium film. Olpin made use of a sodium cell in which the anode was completely insensitive to visible light and found that the stopping potential was not affected by the presence of light of lower frequency. Marx had realized that his results would be affected by a photoelectric emission from the anode and had taken precautions to shield the anode from the incident light by means of a cylinder of black glass, and also by placing the anode behind the cathode where the direct light could not reach it. This did not affect his results however. (The possibility of charges collecting on the glass shield was not mentioned, although this also might cause a similar effect.)

Marx and Meyer[2] have recently published an elaborate mathematical theory of the effect in which it is concluded that the experimental results can be accounted for quantitatively by changes in the space-charge conditions near the cathode. An increase in the density of space charge caused by the additional electrons released by the low-frequency light would cause a loss in energy of the electrons reaching the anode, and hence a decrease in stopping potential. At the present time, however, it appears best to postpone a detailed discussion of the theory until its experimental basis has become more firmly established. The subject is one which would repay further investigation.

[1] A. R. Olpin, *Phys. Rev.*, **35**, 112 (1930).

[2] E. Marx and A. E. H. Meyer, *Phys. Zeits.*, **32**, 153 (1931).

APPENDIX

TABLE I.—VALUES OF PHYSICAL CONSTANTS[1]

Velocity of light	$c = 2.99796 \times 10^{10}$ cm/sec
Mechanical equivalent of heat	$J = 4.185$ abs-joule/cal_{15}
Electronic charge	$e = 4.770 \times 10^{-10}$ e.s.u.
	$e/c = 1.591 \times 10^{-20}$ e.m.u.
Specific electronic charge (spectroscopic)	$e/m = 1.761 \times 10^{7}$ e.m.u./g
	$(e/m)c = 5.279 \times 10^{17}$ e.s.u./g
Planck constant	$h = (6.547 \pm 0.008) \times 10^{-27}$ erg-sec
Avogadro's number	$N = 6.064 \times 10^{23}$ mole^{-1}
Boltzmann constant	$k = 1.3708 \times 10^{-16}$ erg/deg
Mass of electron (spectroscopic)	$m = 9.035 \times 10^{-28}$ g
Mass of electron (deflection)	$m = 8.994 \times 10^{-28}$ g
Wave-length associated with 1 volt	$\lambda_o = hc^2/e = (12336 \pm 5) \times 10^{-8}$ cm-volt
Compton shift at 90 deg	$h/mc = 0.0242$ A.u.
Speed of abs-volt-electron:	
Spectroscopic	$v_e = 5.9346 \times 10^{7}$ cm/sec
Deflection	$v_e = 5.9481 \times 10^{7}$ cm/sec
De Broglie wave-length of abs-volt electron	$h/mv_e = 12.210 \times 10^{-8}$ cm

[1] From R. T. BIRGE, *Phys. Rev., Supplement* **1**, 1 (1929)

SUMMARY OF ILLUMINATING ENGINEERING UNITS AND NOMENCLATURE[1]

1. *Radiant flux* is the rate of energy radiation (irrespective of wave-length) and is measured in ergs per second or in watts. *Radiant intensity* is the radiant flux per unit area.

2. *Luminous flux* is the rate of passage of (visible) radiant energy evaluated by reference to the luminous (visual) sensation produced by it. It is measured in lumens.

3. *Lumen*—the luminous flux emitted in unit solid angle by a uniform point source of one international candle. The total flux F emitted from a point source of I candlepower is then $F = 4\pi I$.

4. *The luminous intensity* of a point source in any direction is the luminous flux emitted in unit solid angle in that direction. The unit is the international candle defined by agreement of the National Standardizing Laboratories of France, Great Britain, and the United States in 1909.

5. *The illumination* at a point on a surface is the density of luminous flux (or flux per unit area) incident at that point. It is measured in lux, phots, or footcandles.

6. *Lux*—the practical unit of illumination—is equivalent to an illumination of 1 lumen per square meter, or it is the illumination at the surface of a sphere 1 meter in radius produced by a uniform point source of 1 international candle at its center. (It is thus equivalent to 1 metercandle.)

[1] Condensed in part from *Trans. Amer. Illum. Eng. Soc.*, **20**, 629 (1925).

7. *Phot*—the illumination equivalent to 1 lumen per square centimeter. Hence 1 phot = 10^4 lux.

8. *Footcandle*—the illumination equivalent to 1 lumen per square foot, or the illumination at the surface of a sphere 1 foot in radius produced by a uniform point source of 1 international candle at its center. One footcandle = 10.764 lux.

9. The illumination at a point at a distance R from a uniform point source of I candlepower is equal to I/R^2 and will be given in lux, phots, or footcandles, when R is expressed in meters, centimeters, or feet, respectively. The illumination at a distance R from a uniform point source emitting F lumens is $F/4\pi R^2$, with the same conventions as to units as before.

10. Incandescent lamps are now commonly rated in lumens rather than in candlepower. The flux in lumens divided by 4π gives the *mean spherical candlepower*. The *efficiency* of a lamp is the ratio of the total flux emitted to the total power consumed, and is therefore expressed in lumens per watt. (Modern gas-filled lamps have an efficiency of about 12 lumens per watt consumed.)

11. *The visibility factor* for radiation of any wave-length is the ratio of the luminous flux at that wave-length to the corresponding radiant flux, and is measured in lumens per watt. The *maximum visibility factor* is obtained at a wave-length of approximately 5500A and has the value 621 lumens per watt. The *relative visibility factor* is the ratio of the visibility factor at any wave-length to the maximum visibility factor. (A curve showing the relative visibility factor as a function of wave-length has been plotted in Fig. 13-1, page 468.)

12. It has become a common practice to rate commercial photoelectric cells by expressing their "yield" (photocurrent per unit light flux[1]) in amperes per lumen. Since two lamps emitting the same *radiant* flux might emit quite different *luminous* flux, it is necessary to specify the particular source of light used (*e.g.*, a tungsten filament at 2700°K). If the radiant flux from a given source, contained in the wave-length range between λ and $\lambda + d\lambda$, is $E(\lambda)d\lambda$, in watts, and if the visibility factor is represented by the function $V(\lambda)$, in lumens per watt, then the total *luminous flux* from the source is given in lumens by

$$F = \int_0^\infty V(\lambda)E(\lambda)d\lambda.$$

But the efficiency of the source, in lumens per watt, is given by $E = F/\phi$, where ϕ is the total *radiant flux*,

$$\phi = \int_0^\infty E(\lambda)d\lambda.$$

If i is the photoelectric yield in amperes per watt, then the yield I in amperes per lumen is given by

$$I = \frac{i}{E} = i\frac{\int_0^\infty E(\lambda)d\lambda}{\int_0^\infty V(\lambda)E(\lambda)d\lambda}.$$

For incandescent lamps the efficiency is often given directly, but it may in principle be computed for *any* source from the above equations.

[1] The radiant flux [or the luminous flux] falling on a cell is equal to the product of the radiant intensity [or illumination] by the area of the intercepted light beam.

TABLE II.—PHOTOELECTRIC ENERGY RELATIONS[1]

Wave-length	Frequency	Energy of quantum	Energy per mol	Electron energy	Electron velocity[2]	De Broglie wave-length[2]	Maximum photo-electric yield[3]
λ (A.u.)	ν (sec^{-1})	$h\nu$ (erg)	$\frac{Nh\nu}{J}\left(\frac{\text{cal}}{\text{mol}}\right)$	$V = \frac{12336}{\lambda}$ (volts)	$v = \sqrt{\frac{2h\nu}{m}}$ (cm/sec)	$\lambda_e = \frac{h}{mv}$ (A.u.)	$Y = \frac{e \times 10^8}{h\nu c}$ (amp/watt)[4]
0.001	2.998×10^{21}	1.96×10^{-5}	2.85×10^{11}	1.23×10^{7}	2.993×10^{10}	9.62×10^{-4}	8.11×10^{-8}
0.01	2.998×10^{20}	1.96×10^{-6}	2.85×10^{10}	1.23×10^{6}	2.87×10^{10}	7.40×10^{-3}	8.11×10^{-7}
0.1	2.998×10^{19}	1.96×10^{-7}	2.85×10^{9}	1.23×10^{5}	1.78×10^{10}	3.29×10^{-2}	8.11×10^{-6}
0.3	9.993×10^{18}	6.54×10^{-8}	9.49×10^{8}	4.11×10^{4}	1.14×10^{10}	5.92×10^{-2}	2.43×10^{-6}
0.5	5.996×10^{18}	3.93×10^{-8}	5.69×10^{8}	2.47×10^{4}	9.01×10^{9}	7.70×10^{-2}	4.05×10^{-6}
1.0	2.998×10^{18}	1.96×10^{-8}	2.85×10^{8}	1.23×10^{4}	6.48×10^{9}	0.110	8.11×10^{-6}
10.0	2.998×10^{17}	1.96×10^{-9}	2.85×10^{7}	1.23×10^{3}	2.09×10^{9}	0.348	8.11×10^{-4}
100.0	2.998×10^{16}	1.96×10^{-10}	2.85×10^{6}	1.23×10^{2}	66.04×10^{7}	1.10	8.11×10^{-3}
1,000.0	2.998×10^{15}	1.96×10^{-11}	2.85×10^{5}	12.34	20.88×10^{7}	3.48	8.11×10^{-2}
1,850 (Hg)	1.621×10^{15}	1.06×10^{-11}	1.54×10^{5}	6.67	15.36×10^{7}	4.74	1.50×10^{-1}
2,000	1.499×10^{15}	9.81×10^{-12}	1.42×10^{5}	6.17	14.76×10^{7}	4.93	1.62×10^{-1}
2,500	1.199×10^{15}	7.85×10^{-12}	1.14×10^{5}	4.93	13.21×10^{7}	5.51	2.03×10^{-1}
2,536 (Hg)	1.182×10^{15}	7.74×10^{-12}	1.12×10^{5}	4.86	13.11×10^{7}	5.55	2.06×10^{-1}
2,700 (Hg)	1.110×10^{15}	7.27×10^{-12}	1.05×10^{5}	4.57	12.70×10^{7}	5.73	2.19×10^{-1}
3,000	9.993×10^{14}	6.54×10^{-12}	9.49×10^{4}	4.11	12.05×10^{7}	6.04	2.43×10^{-1}
3,342 (Hg)	8.971×10^{14}	5.87×10^{-12}	8.52×10^{4}	3.69	11.42×10^{7}	6.37	2.71×10^{-1}
3,500	8.566×10^{14}	5.61×10^{-12}	8.13×10^{4}	3.53	11.16×10^{7}	6.52	2.84×10^{-1}
3,656 (Hg)	8.200×10^{14}	5.37×10^{-12}	7.79×10^{4}	3.37	10.92×10^{7}	6.66	2.96×10^{-1}
4,000	7.495×10^{14}	4.91×10^{-12}	7.12×10^{4}	3.08	10.44×10^{7}	6.97	3.24×10^{-1}
4,350 (Hg)	6.892×10^{14}	4.51×10^{-12}	6.54×10^{4}	2.84	10.01×10^{7}	7.27	3.53×10^{-1}
4,500	6.662×10^{14}	4.36×10^{-12}	6.32×10^{4}	2.74	9.85×10^{7}	7.39	3.65×10^{-1}
5,000	5.996×10^{14}	3.93×10^{-12}	5.69×10^{4}	2.47	9.34×10^{7}	7.79	4.05×10^{-1}
5,500	5.451×10^{14}	3.57×10^{-12}	5.18×10^{4}	2.24	8.91×10^{7}	8.17	4.46×10^{-1}
6,000	4.997×10^{14}	3.27×10^{-12}	4.74×10^{4}	2.06	8.53×10^{7}	8.53	4.86×10^{-1}
6,500	4.612×10^{14}	3.02×10^{-12}	4.38×10^{4}	1.90	8.19×10^{7}	8.88	5.27×10^{-1}
7,000	4.283×10^{14}	2.80×10^{-12}	4.07×10^{4}	1.76	7.89×10^{7}	9.22	5.67×10^{-1}
8,000	3.747×10^{14}	2.45×10^{-12}	3.56×10^{4}	1.54	7.38×10^{7}	9.85	6.49×10^{-1}
10,000	2.998×10^{14}	1.96×10^{-12}	2.85×10^{4}	1.23	6.60×10^{7}	11.02	8.11×10^{-1}
20,000	1.499×10^{14}	$.98 \times 10^{-12}$	1.42×10^{4}	0.62	4.67×10^{7}	15.58	16.21×10^{-1}

[1] A useful chart showing graphically many of these relations has been published by W. E. Deming, *Jour. Opt. Soc. Amer.*, **18**, 50 (1929).

[2] For the first seven values in the table the relativity formulae $m_0c^2\left[\frac{1}{\sqrt{1-\beta^2}} - 1\right] = h\nu$ and $\lambda_e = \left(\frac{h}{m_0v}\right)\sqrt{1-\beta^2}$, were used.

[3] Assuming one electron ejected for each quantum absorbed.

[4] To reduce to coulombs per calorie, multiply by 4.18.

PERIODIC CHART OF THE ELEMENTS WITH ATOMIC NUMBERS AND ATOMIC WEIGHTS

I	II	III	IV	V	VI	VII	VIII or 0	*			
								57 La 138 91	58 Ce 140 25	59 Pr 140 92	
1 H 1.0077							2 He 4 00	60 Nd 144 27	61	62 Sa 150 43	63 Eu .152 0
3 Li 6.939	4 Be 9 02	5 B 10 82	6 C 12 00	7 N 14 008	8 O 16 000	9 F 19 00	10 Ne 20 2	64 Gd 157 26	65 Tb 159.2	66 Dy 162 52	67 Ho 163 4
11 Na 22.997	12 Mg 24.32	13 Al 26 96	14 Si 28.06	15 P 31 024	16 S 32 065	17 Cl 35.458	18 A 39.91	68 Er 167 7	69 Tu 169 4	70 Yb 173 6	71 Lu 175 0
19 K 39.095	20 Ca 40 07	21 Sc 45 10	22 Ti 47.9	23 V 50 96	24 Cr 52 01	25 Mn 54 93	26 Fe 55 84	27 Co 58 97	28 Ni 58 69		
29 Cu 63 57	30 Zn 65 38	31 Ga 69.72	32 Ge 72 38	33 As 74 96	34 Se 79 2	35 Br 79 916	36 Kr 82 9				
37 Rb 85.44	38 Sr 87.62	39 Yt 89.0	40 Zr 91	41 Cb 93.1	42 Mo 96 0	43 Ma	44 Ru 101 7	45 Rh 102 91	46 Pd 106 7		
47 Ag 107 880	48 Cd 112 41	49 In 114 8	50 Sn 118 70	51 Sb 121 77	52 Te 127 5	53 I 126 932	54 Xe 130 2				
55 Cs 132 81	56 Ba 137 37	* 57 La 138 91	72 Hf (178 6)	73 Ta 181 5	74 W 184 0	75 Re	76 Os 190.8	77 Ir 193.1	78 Pt 195 23		
79 Au 197.2	80 Hg 200 61	81 Tl 204 4	82 Pb 207.20	83 Bi 209 00	84 Po (210)	85	86 Rn 222				
87	88 Ra 225 95	89 Ac	90 Th 232.15	91 Pa	92 U 238 17						

* Indicates rare earths. See above

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